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The Aerospace Corporation Computer Programs for the Solution of Multielement Chemical Equilibria

28 JUNE 1962

Prepared by
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Materials Sciences Laboratory
and
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Computation and Data Processing Center

Prepared for DEPUTY COMMANDER AEROSPACE SYSTEMS
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Inglewood, California



LABORATORIES DIVISION • AEROSPACE CORPORATION
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**THE AEROSPACE CORPORATION COMPUTER PROGRAMS FOR THE
SOLUTION OF MULTIELEMENT CHEMICAL EQUILIBRIA**

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El Segundo, California

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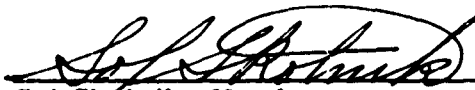
Prepared


S. A. Greene

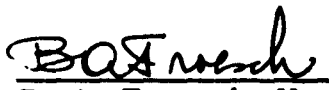
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ABSTRACT

Work has been completed on a generalized method for the analytical solution of complex multielement chemical equilibria under all conditions of pressure, temperature, and mass balance. The programs are written for the IBM 7090 and use a unique technique of majors and minors to guarantee automatic convergence. Variations of the basic solution method are applied to problems in chemical synthesis, thermal stability, and chemical compatibility. The programs are also used to obtain theoretical rocket propellant performance and Mollier diagrams.

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NOMENCLATURE

a	speed of sound
$a_{i,j}$	number of atoms of i th element in j th chemical constituent
A	area
c	specific heat
c^*	characteristic velocity
c_p^t	total specific heat of mixtures
C	molar heat capacity
C_F	thrust coefficient
(c_j)	coefficient matrix of the j th constituent based on element columns (column matrix)
$(C. M.)^{-1}$	inverted coefficient matrix of major products based on element rows
F	free energy
g	gravitational constant
h	specific enthalpy
H	molar enthalpy
ΔH_f	heat of formation
H_o^o	arbitrary constant associated with elements
H_T^o	sum of sensible energy and heat of formation
I_s	specific impulse
J	mechanical equivalent of heat
K	equilibrium constant

\dot{m}	weight flow rate
M	molecular weight
n	moles
N	weight of gas or solid
p	pressure
(p_m)	partial pressure matrix of major products based on element rows (row matrix)
R	gas constant
S	molar entropy
s	specific entropy
T	temperature
u	velocity
v	specific volume
x_g	weight fraction of gases
γ	isentropic exponent
ϵ	area ratio
ρ	density
σ_i	total number of atoms of i th element in system

Superscripts

g	gaseous species
s	condensed species

Subscripts

e	exit conditions
g	gaseous species

p constant pressure
s condensed species
t throat conditions
v constant volume

I. INTRODUCTION

The position of equilibrium in complex (multielement) chemical systems can be computed from first principles. Given selected thermodynamic and thermochemical data associated with reactants and all possible products, the distribution between products and reactants may be uniquely determined at all pressures, temperatures, and stoichiometries. Required data include: heat capacity, entropy, and heat of formation of products and reactants.

The thermodynamic equations that describe systems which contain many elements cannot be solved in closed form and require iterative procedures. These procedures use thermodynamic properties of constituents as input data. It is the purpose of this report to outline the capabilities and applications of a unique computational procedure for the solution of multielement chemical equilibria. The approach uses a technique of majors and minors to assure automatic convergence.

II. OUTLINE OF PROGRAM

Computer programs which solve complex chemical equilibria may be divided into two categories. One type defines equilibria between constituents and their atomic gases; the other, between the constituents which are present in major quantity and the remainder of the products. These are known as methods of minors and majors, respectively.

The former has the advantage of being general in approach, but it is logically complex. It also leads to numerical difficulties at low temperatures where the concentrations of atomic gases become vanishingly small. The latter has the advantage of rapid and certain convergence provided products are selected which are indeed present in major quantity. However, during expansion (and cooling) of equilibrium products, the major products generally change and provision must be made to examine and reselect major products.

The program system described herein combines the flexibility of the minors approach with the convergence advantages of the majors technique. The detailed logic and numerical methods utilized by the program will not be presented here, but they will be the subject of a future report. The calculational procedure is qualitatively the following:

- a) The problem is solved at 3000 K using the minors technique. At 3000 K, the concentration of atomic gases is adequately high and convergence is assured.

Since iterative procedures are utilized, it is necessary to initiate the problem with an estimate of the concentrations of atomic gases. These estimates are stored internally within the program and obviate guesses by the program user. Mass balance and pressure balance equations are applied, and the solution at 3000 K is attained even though the initial atomic gas concentration guesses may be incorrect by factors of 10^{10} .

- b) When initial convergence has been attained, a generalized major product selection routine is given control. A set of major products may be defined as that list of products in which each element appears at least once and which contains the majority of the elements.* As many major products are chosen as there are elemental types. Only gaseous products are considered as candidates. The routine can select a new set of major products at any time during the problem solution.

A. Basic Equations

Some of the basic equations which are solved in the program may be represented by the following:

1. Conservation of Atomic Types (Mass Balance)

$$\sigma_i = \sum_{j=1}^{\beta} a_{i,j} n_j \quad (1)$$

2. Conservation of Pressure

$$P = \sum_{j=1}^{\beta} p_j \quad (2)$$

3. Chemical Equilibrium

$$K_j = \frac{p_j}{\prod_{i=1}^n (p_i)^{a_{i,j}}} \quad (3)$$

*The mathematically rigorous definition will be presented in the previously mentioned, future report.

or using matrix notation for the generalized major product solution

$$\ln K_j = \ln p_j - (C.M.)^{-1} (C_j) (p_m)$$

and, since

$$\Delta F = \Delta H - T\Delta S = -RT \ln K \quad (4)$$

we have

$$\ln K_j = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

4. Conservation of Static Enthalpy

$$h = \sum_{j=1}^{\beta} n_j (H_T^0)_j \quad (6)$$

B. Minors Technique

Using the method of minors, equilibrium constants for constituents are computed in terms of equilibrium between the constituents and their atomic gases. To illustrate, consider the system H, O, OH, and H₂O; equilibria are set up in terms of



The thermodynamic state of the system is fixed by specifying the total amounts of the elements, σ_i , and the total pressure, p . The state of the system can be redefined in terms of pressure, temperature, and concentrations of atomic gases, from which the concentration of the chemical constituents may be computed.

For solution at a given temperature, estimates of the concentration of atomic gases are made from which concentration of constituents follow; the mass balance and total pressure restraints are, of course, taken into account. The equilibrium constants for OH and H₂O are, respectively,

$$\ln K_{OH} = - \left[\frac{(H_T^0)_{OH} - (H_T^0)_H - (H_T^0)_O}{RT} \right] + \left[\frac{(S_T^0)_{OH} - (S_T^0)_H - (S_T^0)_O}{R} \right] \quad (9)$$

$$\ln K_{H_2O} = - \left[\frac{(H_T^0)_{H_2O} - 2(H_T^0)_H - (H_T^0)_O}{RT} \right] + \left[\frac{(S_T^0)_{H_2O} - 2(S_T^0)_H - (S_T^0)_O}{R} \right] \quad (10)$$

From the $\ln K_j$ values, the partial pressures of the j th chemical constituents are computed using Eq. (3). Where the problem is one of combustion at constant pressure, and a flame temperature is sought, the restraint of Eq. (6) must be considered.

Estimates of concentration (and temperature, when necessary) are repeated until convergence is obtained; the iteration controls and sequencing are complex and are beyond the scope of this report.

C. Majors Technique

Each element in a problem requires a major product, and all elements must be represented in the major products at least once. If we select H₂O and H as the major products in the system H, O, OH, and H₂O, then

$$H_2O - H - OH \quad (11)$$



and all products are represented. Equations (9) and (10) then become

$$\ln K_{\text{OH}} = - \left[\frac{(\text{H}_T^{\circ})_{\text{OH}} - (\text{H}_T^{\circ})_{\text{H}_2\text{O}} + (\text{H}_T^{\circ})_{\text{H}}}{RT} \right] + \left[\frac{(\text{S}_T^{\circ})_{\text{OH}} - (\text{S}_T^{\circ})_{\text{H}_2\text{O}} + (\text{S}_T^{\circ})_{\text{H}}}{R} \right] \quad (13)$$

$$\ln K_{\text{H}_2\text{O}} = - \left[\frac{(\text{H}_T^{\circ})_{\text{O}} - (\text{H}_T^{\circ})_{\text{H}_2\text{O}} + 2(\text{H}_T^{\circ})_{\text{H}}}{RT} \right] + \left[\frac{(\text{S}_T^{\circ})_{\text{O}} - (\text{S}_T^{\circ})_{\text{H}_2\text{O}} + 2(\text{S}_T^{\circ})_{\text{H}}}{R} \right] \quad (14)$$

For each nonmajor product, one equilibrium constant needs to be computed.

D. Program Construction

The program is coded in the FORTRAN system and will run on any IBM 7090 EDPM with two on-line channels of at least 7-tape units per channel. The program will consider up to 150 chemical constituents and a maximum of 15 chemical elements per problem.

Each complete program consists of an input or precomputation section, the main computation program, and an output program. A schematic is shown in Fig. 1.

When the program recognizes the chemical elements involved in the problem, the thermodata tape is searched, and all constituents which contain these elements are transferred into core with their corresponding tabular thermodynamic data. A program sophistication allows the program user to specify these constituents which are to be considered, if he so desires.

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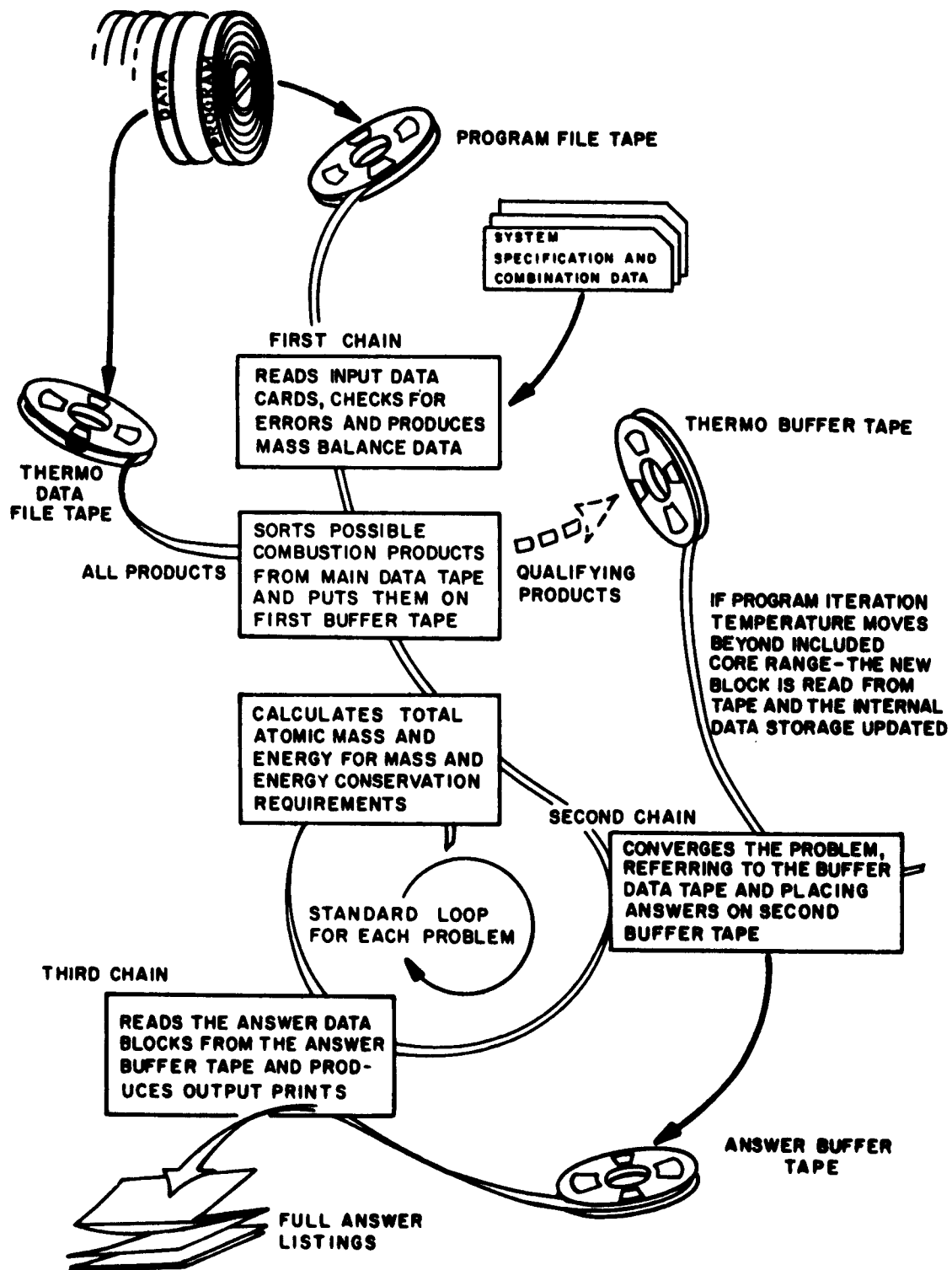


Fig. 1. Program Construction

C

The technique for the solution of chemical equilibria is sufficiently general and independent of application so that it may be incorporated into a variety of special purpose programs. To date, the following computation programs are included:

- 1) Chemical Equilibria,
- 2) Adiabatic Flame Composition,
- 3) Mollier Diagrams, and
- 4) Theoretical Rocket Propellant Performance.

In the FORTRAN programming system, all main programs form chain links and use the same program library and thermodynamic data reference tapes.

The precomputation, or input, program produces the mass balance and data verification sheets. The input data consists of the following information:

- 1) tape unit specification of all tapes including input, output, data library, and program library;
- 2) titles;
- 3) control indicators to select the proper computation program;
- 4) ingredient formulation consisting of name, elements, and coefficients contained and heat of formation of the ingredient;
- 5) combination ratio of ingredients: either moles of each, mole per cent, weight per cent, or mixture ratio;
- 6) specifically included or excluded constituents - optional; and
- 7) any specific data applicable to the computation chain involved, such as enthalpy-entropy boundaries in the Mollier diagram.

All control is internal within each computational program; no computer console settings are required. The only special treatment involved is the loading of the thermodynamic reference tape and the program library. All iteration loops are checked for iteration limits, and an exit procedure is initiated in case of excessive loopings.

C

The programs named above use a basic solution block consisting of four subroutines. These perform the functions of examining major products, building and solving the iteration matrices, and applying the matrix answers. The same subroutines are used in all main calculation programs. The varying types of solutions are obtained by means of control indicators set in the main program and used in the basic block. The basic block can construct and solve any of the following equation systems:

- 1) constant temperature solution of mass balance and pressure balance equations;
- 2) solution of mass and pressure balance equations plus an enthalpy balance-seeks a flame temperature;
- 3) system (1) plus entropy balance (isentropic expansion to assigned pressure);
- 4) constant total enthalpy solution and entropy balance (expansion to assigned mach number);
- 5) constant entropy point solution (to obtain $(\partial p / \partial \rho)_s$ for acoustic velocity determinations); and
- 6) constant pressure point solution (to obtain $(\partial n / \partial T)_p$ for C_p determination).

The only program using all the available matrices is the Rocket Propellant Performance Program. The Chemical Equilibria, Mollier Diagram, and Adiabatic Flame Composition Programs use combinations of (1) and (2).

III. THERMODYNAMIC DATA

From Eqs. (9) and (10) we see that thermodynamic data required for the solution of equilibrium constants include entropy and enthalpy. Since

$$H_T^0 = \Delta H_f^0 + \int_0^T C_p \Delta T \quad (15)$$

we find that H_T^0 is the sum of the sensible enthalpy and chemical energy (heat of formation). Aside from entropy, we require heat capacity and heat of formation data.

Data which are currently available to the Computer Program include the important products of the elements listed in Table 1. While ionic species are not yet included, provision has been made for their incorporation (E is electron). Data on the thermodynamic data tape are composed of heat of formation and heat capacity, enthalpy, and entropy in tabular form from 0 to 6000 K in 100 deg increments. Table 2 illustrates a dump of a constituent contained on the tape.

A. JANAF Thermochemical and Thermodynamic Data Tables

In order to furnish Department of Defense contractors with consistent tables of thermodynamic and thermochemical data, the Joint Army-Navy-Air Force Thermochemical Panel was established in 1960. Under AF 33(616)-6149 and numerous other contracts, thermodynamic data were to be compiled, generated, evaluated, and disseminated in tabular form and on IBM cards. Main contributors include the Dow Chemical Co. (who issue the Tables), National Bureau of Standards, U. S. Bureau of Mines (Bartlesville), and the University of Wisconsin. Table 3 illustrates the format of the tables, while Table 4 shows data documentation observed on their reverse side.

Table 1
Elements Contained on Thermodynamic Data Tape

MAR 29, 1962		
AEROSPACE CORP.		
THERMODYNAMIC DATA TAPES OF AEROSPACE CORP.		
H	34.72039986	
HE	0.	
C		
N	92.21359921	
O	1.88579999	
	2.05544999	
Mg		
AL	233.54669952	
SI	233.62509918	
	250.18759918	
AR		
K	0.	
CA	-20.02899981	
	-44.55899954	
BR		
RB	2.50000000	
ZR	-19.02899981	
	389.66699982	
E		
	61.48099995	
NUMBER OF ELEMENTS=30 NUMBER OF PRODUCTS=278		

Table 2
Example of Tabular Data Contained on Thermodata Tape

MAR 29, 1962

AEROSPACE CORP.

THEMODYN. DATA CENTER OF FIRE
RECORD 240 OF 340 NO. 177742

STATE INDICATOR 1

T	CP	P	S	T	CP	T	CP	M	S
50.00	15.880	-3.987	62.922	•	2000.00	25.752	43.097	131.748	•
100.00	17.621	-2.875	68.230	•	2100.00	25.759	45.672	133.004	•
150.00	20.538	-2.143	75.621	•	2200.00	25.766	48.249	134.203	•
200.00	22.843	0.000	81.000	•	2300.00	25.773	50.826	135.402	•
250.00	24.007	2.393	91.102	•	2400.00	25.785	53.403	136.599	•
300.00	24.611	4.826	96.530	•	2500.00	25.789	56.013	137.754	•
350.00	24.963	7.307	101.051	•	2600.00	25.792	58.559	138.865	•
400.00	25.311	9.788	105.500	•	2700.00	25.796	61.138	139.931	•
450.00	25.659	12.269	110.000	•	2800.00	25.799	63.717	140.918	•
500.00	25.980	14.750	114.500	•	2900.00	25.802	66.296	141.918	•
550.00	26.301	17.231	119.000	•	3000.00	25.804	68.875	142.918	•
600.00	26.622	19.712	123.500	•	3100.00	25.806	71.454	143.918	•
650.00	26.943	22.193	128.000	•	3200.00	25.808	74.033	144.918	•
700.00	27.264	24.674	132.500	•	3300.00	25.810	76.612	145.918	•
750.00	27.585	27.155	137.000	•	3400.00	25.812	79.191	146.918	•
800.00	27.906	29.636	141.500	•	3500.00	25.814	81.770	147.918	•
850.00	28.227	32.117	146.000	•	3600.00	25.816	84.349	148.918	•
900.00	28.548	34.598	150.500	•	3700.00	25.818	86.928	149.918	•
950.00	28.869	37.079	155.000	•	3800.00	25.820	89.507	150.918	•
1000.00	29.190	39.560	159.500	•	3900.00	25.822	92.086	151.918	•
1050.00	29.511	42.041	164.000	•	4000.00	25.824	94.665	152.918	•
1100.00	29.832	44.522	168.500	•	4100.00	25.826	97.244	153.918	•
1150.00	30.153	47.003	173.000	•	4200.00	25.828	99.823	154.918	•
1200.00	30.474	49.484	177.500	•	4300.00	25.830	102.402	155.918	•
1250.00	30.795	51.965	182.000	•	4400.00	25.832	104.981	156.918	•
1300.00	31.116	54.446	186.500	•	4500.00	25.834	107.560	157.918	•
1350.00	31.437	56.927	191.000	•	4600.00	25.836	110.139	158.918	•
1400.00	31.758	59.408	195.500	•	4700.00	25.838	112.718	159.918	•
1450.00	32.079	61.889	200.000	•	4800.00	25.840	115.297	160.918	•
1500.00	32.400	64.370	204.500	•	4900.00	25.842	117.876	161.918	•
1550.00	32.721	66.851	209.000	•	5000.00	25.844	120.455	162.918	•
1600.00	33.042	69.332	213.500	•	5100.00	25.846	123.034	163.918	•
1650.00	33.363	71.813	218.000	•	5200.00	25.848	125.613	164.918	•
1700.00	33.684	74.294	222.500	•	5300.00	25.850	128.192	165.918	•
1750.00	34.005	76.775	227.000	•	5400.00	25.852	130.771	166.918	•
1800.00	34.326	79.256	231.500	•	5500.00	25.854	133.350	167.918	•
1850.00	34.647	81.737	236.000	•	5600.00	25.856	135.929	168.918	•
1900.00	34.968	84.218	240.500	•	5700.00	25.858	138.508	169.918	•
1950.00	35.289	86.699	245.000	•	5800.00	25.860	141.087	170.918	•
2000.00	35.610	89.180	249.500	•	5900.00	25.862	143.666	171.918	•
2050.00	35.931	91.661	254.000	•	6000.00	25.864	146.245	172.918	•
2100.00	36.252	94.142	258.500	•					
2150.00	36.573	96.623	263.000	•					
2200.00	36.894	99.104	267.500	•					
2250.00	37.215	101.585	272.000	•					
2300.00	37.536	104.066	276.500	•					
2350.00	37.857	106.547	281.000	•					
2400.00	38.178	109.028	285.500	•					
2450.00	38.499	111.509	290.000	•					
2500.00	38.820	113.990	294.500	•					
2550.00	39.141	116.471	299.000	•					
2600.00	39.462	118.952	303.500	•					
2650.00	39.783	121.433	308.000	•					
2700.00	40.104	123.914	312.500	•					
2750.00	40.425	126.395	317.000	•					
2800.00	40.746	128.876	321.500	•					
2850.00	41.067	131.357	326.000	•					
2900.00	41.388	133.838	330.500	•					
2950.00	41.709	136.319	335.000	•					
3000.00	42.030	138.800	339.500	•					
3050.00	42.351	141.281	344.000	•					
3100.00	42.672	143.762	348.500	•					
3150.00	42.993	146.243	353.000	•					
3200.00	43.314	148.724	357.500	•					
3250.00	43.635	151.205	362.000	•					
3300.00	43.956	153.686	366.500	•					
3350.00	44.277	156.167	371.000	•					
3400.00	44.598	158.648	375.500	•					
3450.00	44.919	161.129	380.000	•					
3500.00	45.240	163.610	384.500	•					
3550.00	45.561	166.091	389.000	•					
3600.00	45.882	168.572	393.500	•					
3650.00	46.203	171.053	398.000	•					
3700.00	46.524	173.534	402.500	•					
3750.00	46.845	176.015	407.000	•					
3800.00	47.166	178.496	411.500	•					
3850.00	47.487	180.977	416.000	•					
3900.00	47.808	183.458	420.500	•					
3950.00	48.129	185.939	425.000	•					
4000.00	48.450	188.420	429.500	•					
4050.00	48.771	190.901	434.000	•					
4100.00	49.092	193.382	438.500	•					
4150.00	49.413	195.863	443.000	•					
4200.00	49.734	198.344	447.500	•					
4250.00	50.055	200.825	452.000	•					
4300.00	50.376	203.306	456.500	•					
4350.00	50.697	205.787	461.000	•					
4400.00	51.018	208.268	465.500	•					
4450.00	51.339	210.749	470.000	•					
4500.00	51.660	213.230	474.500	•					
4550.00	51.981	215.711	479.000	•					
4600.00	52.302	218.192	483.500	•					
4650.00	52.623	220.673	488.000	•					
4700.00	52.944	223.154	492.500	•					
4750.00	53.265	225.635	497.000	•					
4800.00	53.586	228.116	501.500	•					
4850.00	53.907	230.597	506.000	•					
4900.00	54.228	233.078	510.500	•					
4950.00	54.549	235.559	515.000	•					
5000.00	54.870	238.040	519.500	•					

Table 3
JANAF Thermodynamic Data Table

Be

Beryllium (Be)

(Ideal Gas) Mol. Wt. = 9.013



JANAF THERMOCHEMICAL DATA
Compiled and Calculated by THE DOW CHEMICAL COMPANY, THERMAL LABORATORY, MIDLAND, MICHIGAN



T, °K.	cal. mole ⁻¹ deg. ⁻¹			kcal. mole ⁻¹			Log K _p	
	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	ΔF _f		
0	.000	.000	INFINITE	-	1.481	77.241	77.241	INFINITE
100	4.966	27.118	14.062	-.064	77.728	79.029	-	163.060
200	4.966	30.561	12.999	-.468	78.087	72.177	-	78.667
300	4.966	32.545	12.545	-.000	78.255	69.231	-	50.745
400	4.966	32.576	12.545	.000	78.257	69.175	-	50.392
500	4.966	34.005	12.740	.506	78.315	66.137	-	36.134
600	4.966	35.114	12.108	1.003	78.107	63.093	-	27.576
700	4.966	36.019	11.520	1.500	78.262	60.053	-	21.873
800	4.966	36.785	11.033	1.996	78.187	57.024	-	17.803
900	4.966	37.449	10.632	2.493	78.089	54.007	-	14.753
1000	4.966	38.034	10.311	2.990	77.969	51.004	-	12.385
1100	4.966	38.557	10.070	3.487	77.825	48.015	-	10.493
1200	4.966	39.031	9.807	3.984	77.658	45.042	-	8.949
1300	4.966	39.465	9.520	4.481	77.466	42.085	-	7.664
1400	4.966	39.861	9.212	4.977	77.251	39.146	-	6.581
1500	4.966	40.229	8.890	5.474	77.012	36.223	-	5.654
1600	4.966	40.572	8.551	5.971	76.748	33.318	-	4.854
1700	4.966	40.892	8.196	6.468	76.466	30.431	-	4.167
1800	4.966	41.195	7.827	6.965	76.159	27.567	-	3.576
1900	4.966	41.477	7.445	7.461	75.839	24.735	-	3.052
2000	4.966	41.748	7.051	7.958	75.503	22.044	-	2.584
2100	4.966	42.001	6.645	8.455	75.162	19.504	-	2.164
2200	4.966	42.245	6.228	8.952	74.806	17.115	-	1.785
2300	4.970	42.474	5.801	9.449	74.434	14.878	-	1.442
2400	4.972	42.685	5.365	9.946	74.049	12.789	-	1.130
2500	4.974	42.887	4.920	10.443	73.653	10.841	-	.844
2600	4.977	43.081	4.465	10.941	73.246	8.941	-	.582
2700	4.982	43.266	4.000	11.439	72.829	7.093	-	.342
2800	4.987	43.442	3.525	11.937	72.402	5.293	-	.119
2900	4.997	43.610	3.050	12.435	71.965	3.543	-	.000
3000	5.021	43.771	2.575	12.933	71.518	1.843	-	.000
3100	5.037	43.926	2.100	13.431	71.061	0.193	-	.000
3200	5.057	44.076	1.625	13.929	70.594	-1.507	-	.000
3300	5.081	44.221	1.150	14.427	70.117	-3.207	-	.000
3400	5.109	44.361	0.675	14.925	69.630	-4.907	-	.000
3500	5.142	44.496	0.200	15.423	69.133	-6.607	-	.000
3600	5.179	44.626	-0.275	15.921	68.626	-8.307	-	.000
3700	5.221	44.751	-0.750	16.419	68.109	-10.007	-	.000
3800	5.268	44.871	-1.225	16.917	67.582	-11.707	-	.000
3900	5.320	44.986	-1.700	17.415	67.045	-13.407	-	.000
4000	5.378	45.096	-2.175	17.913	66.498	-15.107	-	.000
4100	5.440	45.201	-2.650	18.411	65.941	-16.807	-	.000
4200	5.508	45.301	-3.125	18.909	65.374	-18.507	-	.000
4300	5.581	45.396	-3.600	19.407	64.797	-20.207	-	.000
4400	5.659	45.486	-4.075	19.905	64.210	-21.907	-	.000
4500	5.741	45.571	-4.550	20.403	63.613	-23.607	-	.000
4600	5.828	45.651	-5.025	20.901	63.006	-25.307	-	.000
4700	5.919	45.726	-5.500	21.399	62.389	-27.007	-	.000
4800	6.014	45.796	-5.975	21.897	61.762	-28.707	-	.000
4900	6.113	45.861	-6.450	22.395	61.125	-30.407	-	.000
5000	6.215	45.921	-6.925	22.893	60.478	-32.107	-	.000
5100	6.320	46.026	-7.400	23.391	59.821	-33.807	-	.000
5200	6.428	46.071	-7.875	23.889	59.154	-35.507	-	.000
5300	6.538	46.111	-8.350	24.387	58.477	-37.207	-	.000
5400	6.651	46.146	-8.825	24.885	57.790	-38.907	-	.000
5500	6.767	46.176	-9.300	25.383	57.093	-40.607	-	.000
5600	6.877	46.201	-9.775	25.881	56.386	-42.307	-	.000
5700	6.993	46.221	-10.250	26.379	55.669	-44.007	-	.000
5800	7.109	46.236	-10.725	26.877	54.942	-45.707	-	.000
5900	7.224	46.246	-11.200	27.375	54.205	-47.407	-	.000
6000	7.340	46.251	-11.675	27.873	53.458	-49.107	-	.000

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Table 4
Data Table Documentation

BERYLLIUM (Be)

(IDEAL GAS)

MOL. WT. = 9.013

$$\Delta H_{FO}^\circ = 77.241 \text{ kcal. mole}^{-1}$$

Ground State Configuration $1s$.

$$\Delta H_f^\circ 298.15 = 78.25 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 32.545 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Multiplicities

$E_1, \text{ cm.}^{-1}$	S_1	$E_1, \text{ cm.}^{-1}$	S_1	$E_1, \text{ cm.}^{-1}$	S_1
0.0	1	67943	15	73089	3
21980	9	68781	5	73141	1
42565	3	69009	3	73520	5
52082	3	69322	1	73608	1
54677	1	69634	9	73803	15
56432	5	70806	15	73867	5
58791	9	71002	5	73930	1
59696	9	71162	3	74071	15
60187	3	71320	1	74117	5
62054	15	71483	9	74163	1
64428	5	71499	1	74269	15
64507	3	72030	15	74301	5
65245	1	72251	5	74416	15
65949	9	72355	3	74443	5
67228	3	72448	1	73430	15
		72882	15		
		73017	5		

Heat of Formation.

Derived from a third law analysis of the vapor pressure data. See Be crystal for references.

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949).

C

These data are used almost exclusively. Data are updated biannually by the Panel, and working meetings are held triannually. Information on almost 550 solid, liquid, and gaseous constituents are available over the 0 to 6000K range or where applicable.

While the tabular data are currently available only to 6000 K, no difficulties are anticipated in extending this range. The Tables may simply be extended by appropriate calculation or a simple routine utilized within the computational program which would extrapolate data to temperatures greater than 6000 K. There is no limit to the maximum temperature, provided ionic^{*} species are considered.

B. Calculation of Thermodynamic Data

The bases for thermodynamic data calculation are standard to statistical mechanics.

Assignments for ideal monoatomic gases include translation and electronic contributions.

For ideal diatomic gases, contributions from translation, rotation, vibration, and electronic transitions are included. When available, spectroscopic constants are utilized; otherwise, appropriate molecular models are used. Anharmonicity corrections are made when adequate data are available.

For linear polyatomic molecules, anharmonic corrections are neglected.

The rigid rotator, harmonic oscillator approximation is utilized for nonlinear polyatomic molecules, and anharmonic corrections are neglected.

Thermodynamic data of condensed phases rest upon either measured or estimated heat capacity data. Heats of transition are either experimentally determined or theoretically estimated and are included in enthalpy and entropy totals.

*The present computation system automatically adds a charge balance equation when ionic species are included in the problem.

C. Determination of Thermochemical Data

Generally, the most important thermodynamic or thermochemical datum is the heat of formation of the constituent. Heats of formation are directly obtained from calorimetric measurements or indirectly from bond energy contributions as estimated from spectroscopic data or calorimetric data. Second law heats are utilized as indirect estimates when necessary.

D. Thermodata Tape Monitor Programs

Programs which maintain and update the thermodata tape are independent of the calculational program. The monitor routines will alter any of the data as given in Table 2 as well as add or delete elements or constituents. In every case of data alteration, the tape identification number is updated as the first action. Where different individuals require their specific data tapes, a number of tapes may be written.

IV. PROGRAM APPLICATIONS

The development of the capability to predict chemical equilibria in systems under analytical or experimental investigation is a valuable adjunct to problems involving chemical synthesis, materials development and testing, laboratory flames, chemical propulsion, and aerodynamics. Whenever possible, thermodynamic calculations should be applied to experimental programs. Consideration of the thermodynamics of the situation can save a great deal of experimentation in terms of a priori analysis.

A. Chemical Synthesis

Experimental attempts to create new molecules through synthesis or high temperature equilibration can be placed on a sound basis by computing the equilibrium composition of products under specified reaction conditions. For illustrative purposes, consider the synthesis of nitric oxide (NO) by the high temperature equilibration (over a catalyst) of an arbitrarily chosen equimolar mixture of nitrogen and oxygen. (See Tables 5 - 10.) Input data to the program include the following which must be specified:

- 1) molar or weight concentrations of reactants;
- 2) total pressure(s) at equilibration; and
- 3) temperature(s) at equilibration.

For an example (only a few points are illustrated), 69 temperatures from 6000 to 300 K were computed at a total pressure of 1 atm in 2.6 min. Between 6000 and 1000 K, temperature increments were 100 K; 1000 to 500 K, increments were 50 K; and 500 to 298.16 K, increments were 25 K.

Table 5 shows the problem definition and mass balance sheets followed by an automatic statement of the products selected for consideration and their heats of formation (Table 6). Tables 7 - 10 show the computed equilibria at various temperatures. Included are their reactant and product concentrations and their individual heat capacities (CP), enthalpies, entropies, and free

Table 5
Problem Definition and Input Verification

AEROSPACE CORPORATION EXAMPLE				CHEMICAL SYNTHESIS	
COMPONENT	WEIGHT PERCENT	MOLES	MOLE PERCENT		
N2	46.680893	1.00000000	50.00000000		
O2	53.319114	1.00000000	50.00000000		
ELEMENTS				MASS BALANCE (MOLES/GM)	
		MOLES			
N		1.0000		0.33324447E-01	
O		1.0000		0.33324447E-01	
INPUT VERIFICATION					
COMPONENT	N2	NUMBER OF ELEMENTS	1	HEAT OF FORMATION (KCAL/MOLE)=	0.
N 2.0000					
COMPONENT	O2	NUMBER OF ELEMENTS	1	HEAT OF FORMATION (KCAL/MOLE)=	0.
O 2.0000					

Table 6
Products Selected from Thermodata Tape
 N_2/O_2

***** PRODUCTS CHOSEN ARE THE FOLLOWING

N	HEAT OF FORMATION	112.96504402
C	HEAT OF FORMATION	59.55014181
NO	HEAT OF FORMATION	21.59791098
NO2	HEAT OF FORMATION	8.09150577
N2	HEAT OF FORMATION	0.00000000
N2O	HEAT OF FORMATION	19.49022865
C2	HEAT OF FORMATION	0.
C3	HEAT OF FORMATION	33.99998856

Table 7
Equilibration of N_2 and O_2 at 6000 K

CHEMICAL SYNTHESIS						
EXAMPLE						
TAPE NO 7/14/61						
PRESSURE (ATM) 1.0000						
TEMPERATURE (DEG K) 6000.00						
SYSTEM ENTHALPY (KCAL/GM) 4.6096						
SYSTEM ENTROPY (KCAL/GR-DEG) 3.1899						
SYSTEM GAS CP 0.33923						
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS	
N	0.11853045	6.1000	144.6299	51.8219	-164.30	
O	0.01824207	5.3234	90.5893	53.6517	-231.51	
NO	0.01134531	9.3128	75.7274	75.1873	-375.3966	
NO2	0.00000000	13.8657	90.1947	86.6732	-429.8443	
N2	0.25080433	9.1652	53.0095	69.9966	-366.9698	
N2O	0.00000039	14.8357	106.7849	91.8208	-155.71	
O2	0.0089743	10.2790	57.5892	74.8898	-117.31	
O3	0.00000000	13.8840	117.2317	95.3925	-112.57	

Table 8
Equilibration of N_2 and O_2 at 3500 K

TAPE 40 7/14/61

EXAMPLE

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CHEMICAL SYNTHESIS

PRESSURE (ATM) 1.0000
TEMPERATURE (DEG K) 3500.00
SYSTEM ENTHALPY (KCAL/GP) 1.7033
SYSTEM ENTROPY (KCAL/GM-DEG) 2.5035
SYSTEM GAS CP 0.31220

PRODCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
N	0.00014004	5.0855	130.8096	48.8670	-40.72750
O	0.25614005	5.0412	77.6383	50.8695	-100.6850
NO	0.06762285	9.0458	52.7646	70.2430	-193.0860
NO2	0.00000057	13.7798	55.6100	79.2188	-221.6557
N2	0.40204521	8.9268	30.3832	65.1239	-197.5503
N2O	0.000000259	14.7067	69.1995	83.8529	-221.745
O2	0.27404840	9.7620	32.3856	69.4687	-210.1
O3	0.00000030	13.8326	82.5691	97.9205	-225

Table 9
Equilibration of N_2 and O_2 at 2700 K

CHEMICAL SYNTHESIS						
EXAMPLE						
PRESSURE (ATM) 1.0000						
SYSTEM ENERGY (KCAL/MOLE) 0.0000						
SYSTEM ENTROPY (KCAL/MOLE) 7.7124						
SYSTEM GAS CP 0.30336						
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS	
N_2	0.00000000	0.00000	0.00000	0.00000	0.00000	
O_2	0.00000000	0.00000	0.00000	0.00000	0.00000	
NO	0.03821791	8.9285	45.5722	67.9105	-137.7862	
NO_2	0.00000073	13.6931	44.6165	75.6531	-159.6468	
N_2O	0.47479122	8.8006	23.2881	62.8229	-146.3338	

Table 10
Equilibration of N_2 and O_2 at 2600 K

CHEMICAL SYNTHESIS					
EXAMPLE					
PRESSURE (ATM) 1.0000					
SYSTEM GAS CP 0.30213					
PRODLCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
NO	0.03321348	8.9103	44.6803	67.5739	-131.0118
NO2	0.00000071	13.6766	43.2490	75.1366	-152.1072
N2	0.97942264	8.7792	22.4091	62.4913	-140.0682

energies (H-TS). System enthalpies, entropies, and heat capacities (frozen equilibria) are also tabulated. From the example, it was concluded that a maximum concentration of NO for the given stoichiometry and pressure would be attained at approximately 3500 K.

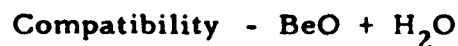
It should be noted that the program can yield adiabatic flame temperatures. Since the enthalpy* of NO at 298.16 K is

$$\begin{aligned}
 h &= \frac{\Delta H_f + H_o^0}{M} \\
 &= \frac{+ 21.60 + [(1)(1.89) + (1)(2.06)]}{30} \\
 &= 0.85 \qquad (16)
 \end{aligned}$$

0.85 kcal/gm, we would calculate that the adiabatic decomposition flame temperature of NO (initially at 298.16 K) is between 2600 and 2700 K (see Tables 9 and 10). Plots of system H vs T over small temperature intervals are linear, and linear interpolation is justified.

B. High Temperature Stability

In many cases it is desired to predict the thermal stability or compatibility of refractories or other materials at elevated temperatures in reactive and inert atmospheres. Tables 11 - 14 illustrate thermodynamic computations of the refractory beryllium oxide in gaseous nitrogen and water vapor. The calculations refer to the stoichiometries



in closed systems and predict the distribution of products which would be

* ΔH_f from Table 6 and H_o^0 from Table 1.

Table 11
Equilibration of BeO and N₂ at 3000 K

EXAMPLE				STABILITY			
PRESSURE (ATM) 1.0000							
SYSTEM GAS CP 0.17128							
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS		
U	0.00039491	5.0042	75.1275	50.0955	-75.1390		
BeO	0.00006144	9.0667	186.9448	66.1427	-11.4834		
Be2O2	0.00027947	19.6799	214.2788	100.0176	-85.7739		
BeO	0.00000000	0.0000	0.0000	0.0000	0.0000		
Be2O6	0.00001945	86.8361	337.6335	222.8522	-330.9231		
NO	0.00042605	8.9773	48.2583	68.8539	-158.3034		
NO2	0.00000000	13.7336	48.7308	77.0980	-182.5632		
U3	0.00000000	13.8047	75.6593	85.1502	-181.7114		
Be	0.00000000	7.5000	152.8641	18.6747	96.8400		
BeO	0.49201348	16.0000	36.7120	33.9904	-65.2593		

Table 12
Equilibration of BeO and N₂ at 2300 K

TAPE 42 3/28/62		EXAMPLE		STABILITY	
		PRESSURE (ATM) 1.0000			
		TEMPERATURE (DEG K) 2300.00			
		SYSTEM ENTHALPY (KCAL/GM) 0.6326			
		SYSTEM ENTROPY (KCAL/GM-DEG) 1.6356			
		SYSTEM GAS CP 0.16412			
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
BE	0.00000017	4.9717	219.1303	62.6955	130.0303
N	0.00000001	4.9724	124.7971	46.1649	17.2378
O	0.00000019	4.9797	71.6350	48.7700	-40.5359
BE0	0.00000001	8.9637	180.6317	63.7470	34.0136
BE2O2	0.00000007	19.5481	200.5430	94.8046	-17.5075
BE3O3	0.00000000	31.1472	196.4684	119.5868	-10.5812
BE4O4	0.00000001	42.7463	232.5267	163.6614	-97.6345
BE5O5	0.00000000	54.6851	273.9357	177.3572	-135.0057
BE6O6	0.00000000	66.3691	290.9825	205.1475	-180.8567
NO	0.00000157	8.8475	42.0162	66.4853	-110.9001
NO2	0.00000000	13.6140	39.1538	73.4635	-129.8122
N2	0.50000184	6.7030	19.1063	61.4195	-121.4385
N2O	0.00000000	14.4644	51.6686	77.7227	-147.0546
O2	0.00000000	9.1940	20.9920	69.4984	-129.0338
O3	0.	13.7319	66.0182	82.1311	-122.8834
BE	COND 0.	7.5000	147.6141	16.6819	109.2457
BE0	COND 0.49999137	13.2650	13.7487	25.3134	-44.4720
BE3O2	COND 0.	36.9400	326.6920	71.5225	140.1003

Table 13
Equilibration of BeO and H₂O at 3000 K

EXAMPLE		COMPATIBILITY			
		PRESSURE (ATM) 1.0000			
		TEMPERATURE (DEG K) 3000.00			
		SYSTEM ENTHALPY (KCAL/GM) 2.4215			
		SYSTEM ENTROPY (KCAL/DEG) 2.5884			
		SYSTEM GAS CP 0.31756			
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
H	0.03150771	4.9681	100.2338	38.8625	-16.3537
BE	0.00002944	5.0206	222.6223	44.8207	-90.5583
O	0.01386432	5.0042	75.1275	50.0955	-75.1590
BEH	0.00000028	9.2248	267.0258	60.7734	84.7055
BEOH	0.00808124	13.3067	159.0052	77.5020	-73.5009
OH	0.04882193	8.7772	89.2372	61.9587	-117.7323
H2	0.07233034	8.8592	90.6492	68.4670	-44.3518
BE(OH)2	0.00024693	25.4312	106.6419	96.5781	-183.2925
H2O	0.34987881	13.1300	43.6948	68.3292	-161.2928
BE0	0.00006698	9.0667	186.9448	66.1427	-11.4834
BE2O2	0.00030470	19.6799	214.2788	100.0176	-85.7739
BE3O3	0.00335041	31.6108	218.3156	127.9807	-394.7865
BE4O4	0.00002782	43.1617	262.6054	156.8762	-202.0335
BE5O5	0.00001566	55.0747	312.3494	191.9531	-283.6607
BE6O6	0.00002120	66.8561	337.6335	222.8522	-330.9231
O2	0.02749057	9.5510	27.5559	67.9797	-176.3832
O3	0.00000000	13.8047	75.6593	85.7902	-181.7114
BE	0.00000000	7.3000	152.8031	10.8767	91.8263
BEH	0.00000000	14.0000	36.7110	33.7904	-87.7894

Table 14
Equilibration of BeO and H₂O at 2300 K

TAPE 42 3/28/62

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COMPATIBILITY

EXAMPLE

PRESSURE (ATM) 1.0000
TEMPERATURE (DEG K) 2300.00
SYSTEM ENTHALPY (KCAL/GM) 1.1691
SYSTEM ENTROPY (CAL/GM-DEG) 2.1177
SYSTEM GAS CP 0.29046

PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
H	0.00071371	4.9681	96.7561	37.5424	10.4085
BE	0.00000000	4.9717	219.1303	42.6955	120.9307
O	0.00023155	4.9797	71.6350	48.7700	-40.5359
BEH	0.00000000	9.0251	260.6341	58.3485	126.4326
BEOH	0.00003609	12.9609	149.7986	74.0095	-20.4231
OH	0.00448672	8.4710	62.1918	59.0639	-73.6551
H2	0.01085225	8.4279	84.5911	46.1712	-21.6026
BE(OH)2	0.00005935	24.6401	88.8786	89.9163	-117.9288
H2O	0.48290771	12.4826	34.7142	64.9241	-114.6113
BE0	0.00000001	8.9637	180.6317	63.7470	34.0136
BE2O2	0.00000008	19.5481	200.5430	94.8046	-17.5075
BE3O3	0.00000310	31.1472	196.4684	119.5868	-78.5812
BE4O4	0.00000001	42.7463	232.5267	143.4614	-97.4345
BE5O5	0.00000000	54.6851	273.9357	177.3572	-133.9857
BE6O6	0.00000000	66.3691	290.9825	205.1475	-180.8567
O2	0.00438121	9.1940	20.9920	65.4904	-129.6358
O3	0.00000000	13.7319	66.0182	82.1311	-122.8834
BE COND	0.49632816	7.5000	147.6141	16.6819	109.2457
BE0 COND	0.49632816	13.2650	13.7487	25.3134	-44.4720

C

observed after an infinite length of time. The tables show that in nitrogen condensed BeO decomposition proceeds through the formation of the gaseous BeO polymers. In water vapor, the gaseous hydroxides play a major role. The partial pressures of the constituents are simply their mole fractions multiplied by the total pressure.

C. Composition of Flames

The computer programs can be of great value to problems which investigate flame phenomena. Input data to the program would consist of oxidizer and fuel stoichiometry and ambient pressure. These conditions would define a premixed flame or a rocket exhaust jet. The actual flame temperature at a given stoichiometry and pressure would easily be calculable from the thermodynamic and thermochemical data of the oxidizer and fuel.

Tables 15 and 16 list the flame compositions of the system tetrafluoroethylene-oxygen ($C_2F_4 + 2O_2$) at ambient pressure. The calculations were made in support of a laboratory program which will investigate the flame in order to give insight into the phenomenology of Teflon ablation in air. One of the surprising results is the extremely high concentration of fluorine atoms. For a given stoichiometry and pressure, this program does not automatically compute the adiabatic flame temperature; these would be hand calculated as shown in Section IV. A., Chemical Synthesis. Oxidizer and fuel enthalpy is 1.00 kcal/gm which yields an adiabatic flame temperature between 2000 - 2100 K.

Calculations, such as those illustrated in Tables 15 and 16, would appear to be an aid toward the prediction of the radiative signatures of rocket exhaust jets. Since the flame composition and temperature is predicted, the concentration of the emitters from first principles has been established. These calculations are, of course, based on thermodynamic equilibrium and do not recognize the existence of excited emitters or other nonequilibrium phenomena.

Table 15
Composition of $C_2F_4 + 2O_2$ Flame at 2100 K

TAPE 43

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COMPOSITION OF FLAME

EXAMPLE

PRESSURE (ATM) 1.0000
TEMPERATURE (DEG K) 2100.00
SYSTEM ENTHALPY (KCAL/GM) 1.0000
SYSTEM ENTROPY (KCAL/GM-DEG) 1.8421
SYSTEM GAS CP 0.29550

PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
C	0.	5.0190	217.4419	47.4136	172.7534
O	0.00049996	6.9780	10.6392	48.3170	-30.8266
F	0.40420459	4.9985	59.5857	48.0112	-41.2377
CO	0.00184855	8.6976	82.2459	62.2309	-48.4391
F2CO	0.20028078	19.3169	38.6264	93.6449	-158.0279
CO2	0.23104442	14.5449	25.5007	74.4294	-131.1354
CF	0.00000000	8.0982	213.7748	66.8969	73.2414
CF2	0.00000057	13.6306	131.9879	82.9792	-42.2689
CF3	0.00017057	19.5379	89.4253	95.4412	-111.0013
CF4	0.03025556	25.2808	42.0275	104.5984	-177.6292
C2	0.	8.8632	395.8423	64.8127	259.7357
C2F2	0.00000000	20.3789	230.3255	95.6084	29.5478
C3	0.	14.5106	490.7830	80.1757	322.3339
O2	0.13124937	9.0840	19.1842	64.6391	-116.6198
O3	0.00000000	13.6970	63.2751	80.8834	-106.5801
F2	0.00044961	9.2294	78.9273	65.1427	-57.8724
C	0.	5.7899	101.1032	10.0039	80.0950

Table 16
Composition of $C_2F_4 + 2O_2$ Flame at 2000 K

TAPE 43 4/27/62		PAGE 41		COMPOSITION OF FLAME	
EXAMPLE		PRESSURE (ATM) 1.0000		SYSTEM GAS CP 0.29409	
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS
F	0.29347803	5.0014	59.0857	47.7290	177.4884
CO	0.00062659	8.6636	81.3777	44.0742	-26.0869
F2CO	0.25186038	19.2632	36.6973	47.7672	-36.4487
				61.8074	-42.2372
				92.7037	-148.7101
CF3	0.00012941	19.5045	87.4732	94.4888	-101.5044
CF4	0.06008898	25.2259	39.5021	103.3663	-167.2305
C2	0.	8.8390	394.9572	64.3808	266.1956
				94.6152	38.0594
				10.4682	310.3165
				64.2172	-110.1198
				80.2157	-98.5249
O3	0.00000000	15.6757	61.9065	64.6930	-51.3804
F2	0.00038378	9.2063	78.0056	9.7202	81.0827
C	0.	5.7577	100.5232		
SOLID					

For the premixed flame, the specification of oxidizer and fuel stoichiometry is reasonable since one expects and observes predicted flame temperatures, radiation, and compositions. However, many processes of interest to the aerospace sciences, such as ablation, must be approximated by a diffusion flame. There is transport of material through the boundary layer, and the flame stoichiometry is not well defined. However, flame temperatures near the theoretical maximum are often observed in diffusion flames although there is no true final flame temperature.

D. Problems Which Contain Many Elements

Tables 17 - 19 illustrate a problem which contains six elements. As seen from the Tables, condensed phases may appear and disappear. Computation time is somewhat increased over that with fewer elements; there are no increased computational difficulties.

E. Mollier Diagrams

Isobaric and isothermal curves on an enthalpy-entropy plane for a given stoichiometry result in a Mollier diagram. Such diagrams are of general utility in power-plant design and thermodynamic analysis. Mollier diagrams are usually presented for single constituents, but the computer routines described in this report are general in nature. Thus, data for the Mollier diagrams can be easily and automatically computed for systems which contain numerous constituents.

Printouts from the current Mollier Diagram Program are illustrated in Tables 20 - 22 and are produced at various pressure and temperature intervals specified by the program user. In practice, points are generated by computing points at equally spaced temperatures along an isobar. When computations have been completed for a temperature range and pressure, the program proceeds to the next pressure. The following data are printed out at each pressure and temperature:

Table 17
Equilibration of ClO_3F and LiBH_4 at 6000 K

MANY ELEMENTS

EXAMPLE

PRESSURE (ATM) 1.0000

SYSTEM GAS CP 0.47670

PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	M-TS
B	0.03563164	5.1684	338.7987	51.5967	29.2183
O	0.26133049	5.3234	90.5893	53.6947	-231.3391
F	0.07563834	4.9721	79.0044	53.2406	-240.6390
Li	0.00001112	9.7471	175.6426	65.8729	-19.5748
H	0.00000010	19.7094	183.3224	106.8963	-458.8555
OH	0.00069825	9.3715	95.6000	67.6558	-310.3347
Li2O2	0.00000000	31.4434	333.9850	136.8087	-486.8670
N2O	0.00000009	13.8585	84.9382	77.8258	-382.0164
BM3	0.00000000	19.6700	399.4451	91.0485	-146.8459
LiF	0.00112163	9.7552	135.5407	74.3703	-310.6008
LiCl	0.00041737	9.7329	143.2809	77.7841	-323.4235
Li2	0.00000209	10.8840	368.2439	75.5337	-84.9585
Li3F3	0.00000000	31.7447	305.3110	159.1736	-649.7306
BO	0.02203544	9.1702	232.7430	73.3037	-207.0791
BOF	0.00019269	14.8558	147.9871	94.9632	-421.7923
				97.7446	-406.9387

Table 17 (continued)
Equilibration of ClO_3F and LiBH_4 at 6000 K

BF	0.01691030	9.3626	212.1393	73.3251	-227.0112
BFCL	0.00000000	14.8719	215.9025	96.8694	-365.3140
BFCL2	0.00000000	19.8351	172.4157	124.1388	-572.4171
BF2	0.00000019	14.0568	185.3677	91.4544	-363.3589
BF2CL	0.00000000	19.8772	140.4777	113.3634	-279.3247
BF3	0.00000000	19.8134	186.5409	113.8400	-374.3003
BCL	0.00008159	9.5003	275.3773	77.3523	-106.1364
BCL2	0.00000000	14.8867	248.5889	100.0540	-351.7353
BCL3	0.00000000	19.8487	204.1350	125.5247	-549.0134
B2	0.00000092	9.5540	601.4428	74.3603	155.2807
B2O2	0.00000018	20.7809	356.3155	112.7478	-328.1879
B2O3	0.00000000	25.4933	284.3738	124.7708	-494.2519
B3O3F3	0.	49.5572	329.3833	211.4278	-946.1523
B3O3CL3	0.	49.5742	416.6441	218.7822	-896.0490
CL0	0.00000553	9.5990	84.8461	80.6010	-398.7600
O2	0.00017820	10.2790	57.5892	74.8898	-391.7494
O3	0.00000000	13.8840	117.2317	95.3923	-400.1292
CLF	0.00000079	9.7638	76.8042	78.8038	-305.8145
F2	0.00000002	9.9366	116.3538	75.1599	-374.8701
CL2	0.00000051	9.6721	62.8723	80.3121	-419.0002
LI0H	0.	20.7400	172.6040	73.5736	-268.8375
LI	0.	6.2920	169.4127	28.5358	-1.8018
LIH	0.	15.3100	108.4440	58.2838	-224.7908
LI2CL	0.	14.4008	124.2758	95.3275	-233.8099
LI2C	0.	23.0000	261.9430	78.9050	-211.4089
B	0.	7.5000	219.9530	21.9231	86.4147
B2O3	0.	32.0000	234.9160	106.4809	-403.9691

Table 18
Equilibration of ClO_3F and LiBH_4 at 1200 K

TAPE 43 4/2/62		EXAMPLE		PAGE 49		MANY ELEMENTS	
		PRESSURE (ATM) 1.0000		TEMPERATURE (DEG K) 1200.00			
		SYSTEM ENTHALPY (KCAL/GM) 1.0358		SYSTEM ENTROPY (KCAL/DEG) 1.6277			
		SYSTEM GAS CP 0.20548					
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	H-TS		
H	0.00000000	4.9683	91.2911	34.3182	50.3189		
Li	0.00000000	4.9683	173.4653	40.0613	125.3917		
O	0.	4.9683	314.7809	43.5683	262.4990		
F	0.00000000	4.9898	66.1561	45.5292	11.5211		
Cl	0.00000000	5.0521	55.0689	45.2013	0.8274		
BH	0.00000000	5.2779	30.7708	46.9301	-17.5982		
LiBH	0.	8.1946	204.2448	51.8538	166.0202		
LiBH4	0.00000002	13.1227	128.8133	66.9830	48.4337		
BH3	0.	8.1946	331.3595	51.3183	269.7176		
M802	0.00081556	17.0794	91.2904	76.5195	-0.5331		
OH	0.00000012	7.5478	53.3203	53.8497	-11.2993		
HF	0.00000000	7.4023	7.4023	51.3293	-53.1029		
H2O	0.00000000	7.8194	58.2348	54.6324	-41.3468		
Li2O2H2	0.00000000	7.4045	55.8436	41.0358	26.8818		
M20	0.00000000	26.6628	188.1199	88.8069	81.5516		
BH3	0.38153469	10.4343	21.9440	57.4403	-46.9844		
	0.	15.9753	308.4417	61.1935	235.0095		
	0.	15.9753	78.1377	102.8192	-53.0972		
	0.00000000	15.9753	148.1379	148.0906	-37.5916		
LiF	0.00000000	8.4315	153.8478	60.5314	81.0101		
LiCl	0.00000044	8.9230	90.4362	59.4121	19.1417		
Li2	0.00633576	9.0041	98.1639	62.8035	22.1998		
	0.	9.3019	319.7529	59.6012	248.2314		
	0.	17.0794	238.9194	71.3288	152.3191		
	0.00000000	19.0784	124.8736	89.5234	24.2448		
Li3F3	0.00000000	18.0000	141.1633	95.3319	35.2858		
BH	0.00000183	30.3756	153.8976	108.6002	23.5773		
BH	0.	8.3247	189.8064	59.0628	118.9310		
BH3	0.00027346	13.9127	77.5220	71.5014	-8.2797		
			148.5273	79.2863	19.8173		

Table 18 (continued)
Equilibration of ClO_3F and LiBH_4 at 1200 K

BF	0.00000000	8.6199	168.3780	58.7919	97.0278
BFCL	0.00000000	14.1661	145.1125	73.2532	57.2086
BFCL2	0.00000035	19.1023	77.8035	92.5397	-33.2441
BF2	0.00000000	13.8492	114.9162	68.0042	33.3112
BF2CL	0.00007474	18.8438	46.1376	88.5018	-88.0000
BF3	0.00584036	18.5562	14.5076	82.5259	-64.1200
BCL	0.	8.8948	230.9861	62.5872	197.0018
BCL2	0.	14.4888	177.4614	76.2717	85.9353
BCL3	0.00000000	19.3081	109.3066	93.8193	-3.2766
B2	0.	8.8219	556.9736	59.5924	485.4627
B2O2	0.	18.1277	258.0459	80.0813	103.9408
B2O3	0.00000002	22.9840	163.5131	89.7321	58.0000
B3O3F3	0.00136311	44.8039	94.0041	133.0970	-45.7823
B3O3CL3	0.00000000	47.2005	180.6678	140.0596	12.5964
ClO	0.00000000	8.9060	40.1783	65.7610	-38.7349
O2	0.00000019	8.5270	11.2245	59.7364	-60.4592
O3	0.	13.2875	51.0844	73.3137	-44.3000
CLF	0.00000000	8.9659	31.4378	83.8193	-1.3000
F2	0.	8.9553	70.7297	60.0525	-1.3000
CL2	0.00000433	9.0158	17.9096	65.3691	-60.5334
LiOH	0.	20.7400	73.0520	40.1916	24.8221
Li	0.	6.8680	137.8284	17.8361	116.4251
LiF	0.17017145	13.3100	28.6726	23.8203	-2.2000
LiCl	0.07085697	14.4000	55.1550	36.1516	11.7800
Li2O	0.	22.0008	139.0024	33.4709	96.0000
B	0.	6.5010	179.8204	8.1611	170.0271
B2O3	0.11341250	32.0000	81.3160	54.9789	15.3413

Table 19
Equilibration of ClO_3F and LiBH_4 at 500 K

TAPE 43 4/2/62		EXAMPLE		MANY ELEMENTS	
		PRESSURE (ATM) 1.0000			
		SYSTEM GAS CP 0.24322			
PRODUCT	MOLE FRACTION	CP	ENTHALPY	ENTROPY	M-TS
Li	0.	4.9691	311.3030	39.2104	291.6930
O	0.	5.0808	42.6440	41.1312	42.0704
F	0.	5.2822	51.4754	40.6924	31.1292
LiH	0.	7.1064	325.9011	44.6768	303.8327
LiBH	0.	12.9458	80.5017	63.2914	48.8560
LiBH ₂	0.	7.0492	48.2632	47.5548	24.4048
Li ₂ O	0.	19.3344	171.3033	68.3330	137.2128
H ₂ O	0.29436745	8.4156	15.3554	49.3337	-9.3115
BH ₃	0.	10.0476	299.0417	49.8290	274.1272
LiF	0.	8.1887	84.3708	51.8719	50.4349
LiCl	0.00000000	8.5204	91.9785	55.0970	64.4300
Li ₂	0.	8.9430	313.3443	51.8133	287.5416
Li ₃ F ₃	0.	26.1724	133.4943	83.3525	91.8101
BO	0.	7.2301	104.3114	52.2633	150.1797
BOF	0.	11.8042	68.3289	60.1335	30.2621

Table 19 (continued)
Equilibration of ClO_3F and LiBH_4 at 500 K

BF	0-	7.5812	162.6226	51.6611	136.7921
BFCL	0-	11.9531	135.7296	61.6567	104.9013
BFCL2	0.00000000	16.6498	65.0125	76.6948	26.6651
BF2	0-	10.9861	105.9355	56.9534	77.4588
BF2CL	0.00000000	15.8166	33.6833	73.1164	-2.8798
BF3	0.00000170	14.9659	7.4144	67.4265	-31.3948
BCL	0-	8.2484	224.9146	55.8336	197.3878
BCL2	0-	13.0347	167.6518	64.0924	135.6056
BCL3	0-	17.2981	96.2489	77.6117	57.4430
B2	0-	7.9795	551.0082	52.1846	524.9159
B2O2	0-	15.8438	249.8022	64.7613	213.2516
B2O3	0-	16.5428	194.1849	72.1391	113.0093
B3O3F3	0.00000004	37.5451	63.4297	95.4347	15.7123
B3O3CL3	0-	39.1973	149.5135	101.5925	98.7172
CL0	0-	8.2262	34.1088	58.2120	5.0028
O2	0-	7.4310	5.5652	52.7300	-20.7997
O3	0-	11.2093	82.2817	62.4087	112.0893
CLF	0-	8.3619	25.5148	54.1987	-2.3694
F2	0-	8.1918	64.6514	52.4981	38.4084
CL2	0.00000001	8.6236	11.6940	57.6192	-17.1156
LI0H	0-	15.2010	54.5124	16.9772	46.0238
LI	LIQUID	7.0650	132.9503	11.7501	127.0753
LIF	COND	11.8318	19.2206	18.1931	127.1247
LiCL	COND	14.4008	45.8758	23.5448	35.3026
LI2O	COND	16.4278	125.3189	16.7000	116.9608
B	SOLID	4.4970	175.8348	3.3012	174.1843
B2O3	COND	21.0000	54.6790	22.2682	43.5449

Table 20
Input Verification of Mollier Diagram Program System Is $C_2N_2F_8/NH_4ClO_4/LiAlH_4$

COMPONENT	C2 N2 F8	NUMBER OF ELEMENTS	3 HEAT OF FORMATION (KCAL/MOLE)=	0.
COMPONENT				
LI-AL-H4				
LI1.0000 AL1.0000 H 4.0000				

Table 21
Products Selected from Thermodata Tape
 $C_2N_2F_8/NH_4ClO_4/LiAlH_4$

H	HEAT OF FORMATION	52.09024620
LI	HEAT OF FORMATION	37.35074234
F	HEAT OF FORMATION	18.96126733
AL	HEAT OF FORMATION	78.59360123
CL	HEAT OF FORMATION	25.94370773
HCN	HEAT OF FORMATION	31.18430339
CHO	HEAT OF FORMATION	-1.14804840
MFCO	HEAT OF FORMATION	-91.51711845
NH	HEAT OF FORMATION	81.27510738
MNO	HEAT OF FORMATION	14.08901262
CH	HEAT OF FORMATION	10.05754995
HCL	HEAT OF FORMATION	-22.05139647
H2	HEAT OF FORMATION	0.
LI2O2H2	HEAT OF FORMATION	-148.77707100
CH2F2	HEAT OF FORMATION	-102.95657539
C2H2	HEAT OF FORMATION	54.12521935
NH2	HEAT OF FORMATION	42.67289829
NH3	HEAT OF FORMATION	-11.06597392
CH4	HEAT OF FORMATION	-17.92509698
LIO	HEAT OF FORMATION	12.88809967

Table 21 (continued)
Products Selected from Thermodata Tape
 $C_2N_2F_8/NH_4ClO_4/LiAlH_4$

LiC	HEAT OF FORMATION	-44.5220385
Li2	HEAT OF FORMATION	58.50184937
Li2O	HEAT OF FORMATION	-37.60570145
Li2F2	HEAT OF FORMATION	-215.64468846
	HEAT OF FORMATION	-1182.78728093
	HEAT OF FORMATION	-246.8220385
	HEAT OF FORMATION	96.75431481
FCN	HEAT OF FORMATION	-12.83328724
CLCN	HEAT OF FORMATION	34.13969326
CO	HEAT OF FORMATION	-26.45284939
	HEAT OF FORMATION	-66.09119892
CO2	HEAT OF FORMATION	74.74216461
CF	HEAT OF FORMATION	-71.77709389
CCL3F	HEAT OF FORMATION	-211.0000000
	HEAT OF FORMATION	-20.17200000
	HEAT OF FORMATION	172.85323187
CF3Cl	HEAT OF FORMATION	-171.93898773
CF4	HEAT OF FORMATION	-217.95817184
ALC	HEAT OF FORMATION	212.05557278
	HEAT OF FORMATION	146.84237184
	HEAT OF FORMATION	-51.56782265
AL2C2	HEAT OF FORMATION	-30.89197540
C3	HEAT OF FORMATION	189.82765579
	HEAT OF FORMATION	-107.63692780
ALN	HEAT OF FORMATION	-0.00000024
N2	HEAT OF FORMATION	19.89022865
N2O	HEAT OF FORMATION	87.84337746
	HEAT OF FORMATION	-36.87511826
AL2O	HEAT OF FORMATION	25.45765376
ClO	HEAT OF FORMATION	0.
O2	HEAT OF FORMATION	100.00000000

Table 21 (continued)
Products Selected from Thermodata Tape
 $C_2N_2F_8/NH_4ClO_4/LiAlH_4$

DES	HEAT OF FORMATION	33.99998856
ALF	HEAT OF FORMATION	-58.90781593
ALCLF	HEAT OF FORMATION	-119.01047516
ALFCL2	HEAT OF FORMATION	-180.70163155
CLF	HEAT OF FORMATION	-12.63953829
F2	HEAT OF FORMATION	-0.00000095
ALF2	HEAT OF FORMATION	-155.85352516
ALF2CL	HEAT OF FORMATION	-234.49999237
ALF3	HEAT OF FORMATION	-283.70128632
ALCL	HEAT OF FORMATION	-10.20645714
ALCL2	HEAT OF FORMATION	-16.98002060
ALCL3	HEAT OF FORMATION	-137.92539706
AL2	HEAT OF FORMATION	106.14785004
CL2	HEAT OF FORMATION	-0.00004923
LI OH	COND	-116.66994953
LI	LIQUID	-0.00000381
LI OH2	COND	-281.31109219
LI2	COND	136.77592049
LI2	LIQUID	94.46419068
LI2O	COND	-143.04864693
LI3N	COND	-51.57710266
C	SOLID	-0.00000191
AL	SOLID	-74.97999922
AL2O3	COND	-406.40654469
ALF3	COND	-355.20355988
AL	COND	-0.00000191
ALCL3	LIQUID	-162.33645058

Table 22
Printout of Mollier Diagram Program

AEROSPACE CORPORATION					
EXPERIMENTAL PROBLEM					
.....					
COMPONENT	WEIGHT PERCENT	MOLES	MOLE PERCENT		
C2 M2 F8	25.000000	1.0000000	7.83635980		
MMA CLO4	29.999999	2.08384553	16.32976317		
LI-AL-H4	44.999999	9.6771816	75.83387756		
.....					
ELEMENTS			MOLES	MASS BALANCE (G/GM)	
H	3.6865	4.21359318	107	2	0.57641358E-01
LI	0.7583	4.17358738	107	3	0.11657063E-01
C	0.1567				0.24505240E-02
N	0.3200				0.50037806E-02
O	0.6532				0.10213026E-01
F	0.6269				0.98920960E-02
AL	0.7583				0.11657063E-01
CL	0.1633				0.25532567E-02
999.999992	6000.000000	12.97377777	107	2	
999.999992	5900.000000	12.73574269	107	3	
999.999992	5800.000000	12.49943606	107	4	
999.999992	5700.000000	12.25521221	107	5	
999.999992	5600.000000	11.99239616	107	6	
999.999992	5500.000000	11.70104063	107	7	
999.999992	5400.000000	11.42306077	107	8	
999.999992	5300.000000	11.13930571	107	9	
999.999992	5200.000000	10.85593784	107	10	
999.999992	5100.000000	10.56346641	107	11	
999.999992	5000.000000	10.26595883	107	12	
999.999992	4900.000000	10.01015544	107	13	
999.999992	4800.000000	9.74322355	107	14	
999.999992	4700.000000	9.46773396	107	15	
999.999992	4600.000000	9.18399878	107	16	
999.999992	4500.000000	8.89259859	107	17	
999.999992	4400.000000	8.59400000	107	18	
999.999992	4300.000000	8.28858856	107	19	
999.999992	4200.000000	7.97696500	107	20	
999.999992	4100.000000	7.64869844	107	21	
999.999992	4000.000000	7.30500000	107	22	

Table 22 (continued)
Printout of Mollier Diagram Program

ALN	SOLID	PRESENT			
AL203	COND	PRESENT			
999.999992	1650.000000	h.49678042	1.94306967	107	49
LIF	COND	PRESENT			
LTCL	LIQUID	PRESENT			
ALN	SOLID	PRESENT			
AL203	COND	PRESENT			
999.999992	1600.000000	h.45473081	1.91443532	107	50
LIF	COND	PRESENT			
LTCL	LIQUID	PRESENT			
ALN	SOLID	PRESENT			
AL203	COND	PRESENT			
999.999992	1500.000000	h.27145827	1.79521561	107	54
LIF	COND	PRESENT			
LTCL	LIQUID	PRESENT			
ALN	SOLID	PRESENT			
AL203	COND	PRESENT			
999.999992	1350.000000	h.18825179	1.73466489	107	55
LIF	COND	PRESENT			
LTCL	LIQUID	PRESENT			
ALN	SOLID	PRESENT			
AL203	COND	PRESENT			
999.999992	1300.000000	h.10526317	1.67208366	107	56
LIF	COND	PRESENT			
LTCL	LIQUID	PRESENT			

Table 22 (continued)
Printout of Mollier Diagram Program

999.999992	625.000000	3.42817162	1.18371151	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	608.000000	2.81546102	1.14330469	101	10
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	575.000000	2.04153100	1.14330469	101	10
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	542.000000	1.25415100	1.14330469	101	10
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	509.000000	0.46515100	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	476.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	443.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	410.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	377.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	344.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	311.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	278.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	245.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	212.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	179.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	146.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	113.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	80.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	47.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				
999.999992	14.000000	0.00000000	1.14330469	101	11
LIF	COND PRESENT				
LICL	LIQUID PRESENT				
ALN	SOLID PRESENT				
HL203	COND PRESENT				
ALF3	COND PRESENT				

<u>Column</u>	<u>Datum</u>
1	Pressure
2	Temperature
3	Enthalpy
4	Entropy
5	Indicator
6	Point Number

When condensed phases appear, the program notes their presence and identifies them (see Table 22).

The subscript COND refers to a constituent whose thermodynamic data over the range 0 to 6000 K is associated with both solid and liquid phases. The data list the melting point to the nearest 100 deg, and the entropy, heat capacity, and enthalpy are discontinuous. System composition data are deleted in order to reduce the amount of output but may be produced as an option. The temperature interval selected for each isobar is identical, facilitating the construction of isotherms on the diagram.

Applications of Mollier diagrams of complex systems are numerous. In the aerospace sciences, obvious application involves determination of theoretical rocket propellant performance and the solution of a host of aerodynamic problems. Most important in the latter case is ablation and the calculation of the thermodynamic and transport properties of flowing, reacting gas mixtures. Since the viscosity and thermal conductivity of a gas mixture is of importance, gas composition must be known before its transport properties can be computed. The ability to treat flow with chemical reaction is mandatory for the solution of contemporary aerodynamic problems.

While each point computed by the Mollier Diagram Program is an equilibrium one, shifting equilibrium parameters such as heat capacity, isentropic exponent, and speed of sound necessary for some aerodynamic calculations are not computed. The program could be modified to compute these

parameters, but computer time would be increased sharply. However, the following section will illustrate how the parameters may be derived from the current program which will be modified slightly.

F. Calculation of the Velocity of Sound

The velocity of sound is

$$a = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s} = \sqrt{\frac{p}{\rho} \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_s} \quad (17)$$

and γ the isentropic exponent is

$$\gamma = \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_s = - \frac{v}{p} \left(\frac{\partial p}{\partial v}\right)_s \quad (18)$$

Using the Bridgman formulas, Eq. (18) is

$$\gamma = - \frac{v}{p} \frac{\frac{C_p}{T}}{\frac{C_p}{T} \left(\frac{\partial v}{\partial p}\right)_T - \left(\frac{\partial v}{\partial T}\right)_p^2} \quad (19)$$

Since

$$pv = \frac{RT}{M} \quad (20)$$

differentiation yields

$$p dv + v dp = \frac{R}{M} dt - \frac{RT}{M^2} dM \quad (21)$$

and substitution in Eq. (19)

$$\gamma = \frac{c_p}{c_p \left[1 + \left(\frac{\partial \ln M}{\partial \ln p} \right)_T \right] - \frac{R}{M} \left[1 - \left(\frac{\partial \ln M}{\partial \ln T} \right)_p \right]^2} \quad (22)$$

where c_p , the shifting equilibrium heat capacity, is

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p \cong \frac{h_2 - h_1}{T_2 - T_1} \quad (23)$$

For a nonreacting gas mixture (frozen equilibrium)

$$\left(\frac{\partial \ln M}{\partial \ln p} \right)_T = \left(\frac{\partial \ln M}{\partial \ln T} \right)_p = 0 \quad (24)$$

and Eqs. (22) and (17) are reduced to

$$\gamma = \frac{c_p}{c_p - \frac{R}{M}} \quad (25)$$

and

$$a^2 = p v \gamma = \frac{RT}{M} \gamma \quad (26)$$

Molecular weight changes are primarily caused by reassociation of high temperature species; the degree of dissociation is related exponentially to temperature and is much less sensitive to pressure. At static temperatures below, e. g., 1500 K, molecular weight changes become negligible and Eq. (25) may be utilized. At temperatures below approximately 1500 K, frozen and shifting equilibrium parameters are essentially identical. Table 23 illustrates values for frozen and shifting γ in the oxygen/hydrogen system.

Table 23
Comparison of Frozen and Shifting γ in O_2/H_2 Mixtures (60 psia)

T(°K)	γ	
	Shifting	Frozen
1183	1.3395	1.3396
1514	1.3077	1.3079
2089	1.2550	1.2649
2329	1.2267	1.2510
2828	1.1605	1.2265
3015	1.1386	1.2182
3217	1.1174	1.2077

In order to evaluate the shifting equilibrium isentropic exponent and the speed of sound for areas on a Mollier diagram, we need information on

- 1) enthalpy
- 2) molecular weight
- 3) pressure
- 4) temperature
- 5) volume

These will be tabulated for each point; for a given isobar, the molecular weight, enthalpy, and specific volume will be found on the printout. The speed of sound and isentropic exponent may then be evaluated graphically.

A section of a Mollier diagram is illustrated in Fig. 2, and we wish to calculate the isentropic exponent in the area of p_1 and T_1 from Eq. (22). Evaluation of $(\partial \ln M)/(\partial \ln p)_T$ and $(\partial \ln M)/(\partial \ln T)_p$ would be made over the interval $p_0, T_1 - p_2, T_1$ and $p_1, T_2 - p_1, T_0$, respectively, as $(\Delta \ln M)/(\Delta \ln T)_p$. c_p is simply read from the printout as the difference in h between $p_1, T_2 - p_1, T_0$. For the speed of sound we need, in addition, pv at p_1, T_1 . Since the data are printed out along an isobar

$$v = \frac{RT}{Mp} \quad (27)$$

Use of Correct M When System Contains Condensed Phases

Let

$$\gamma = \frac{c_p}{c_v} \quad (28)$$

and for a system which contains a condensed phase

$$\gamma = \frac{N_g c_p^g + N_s c_p^s}{N_g c_v^g + N_s c_v^s} \quad (29)$$

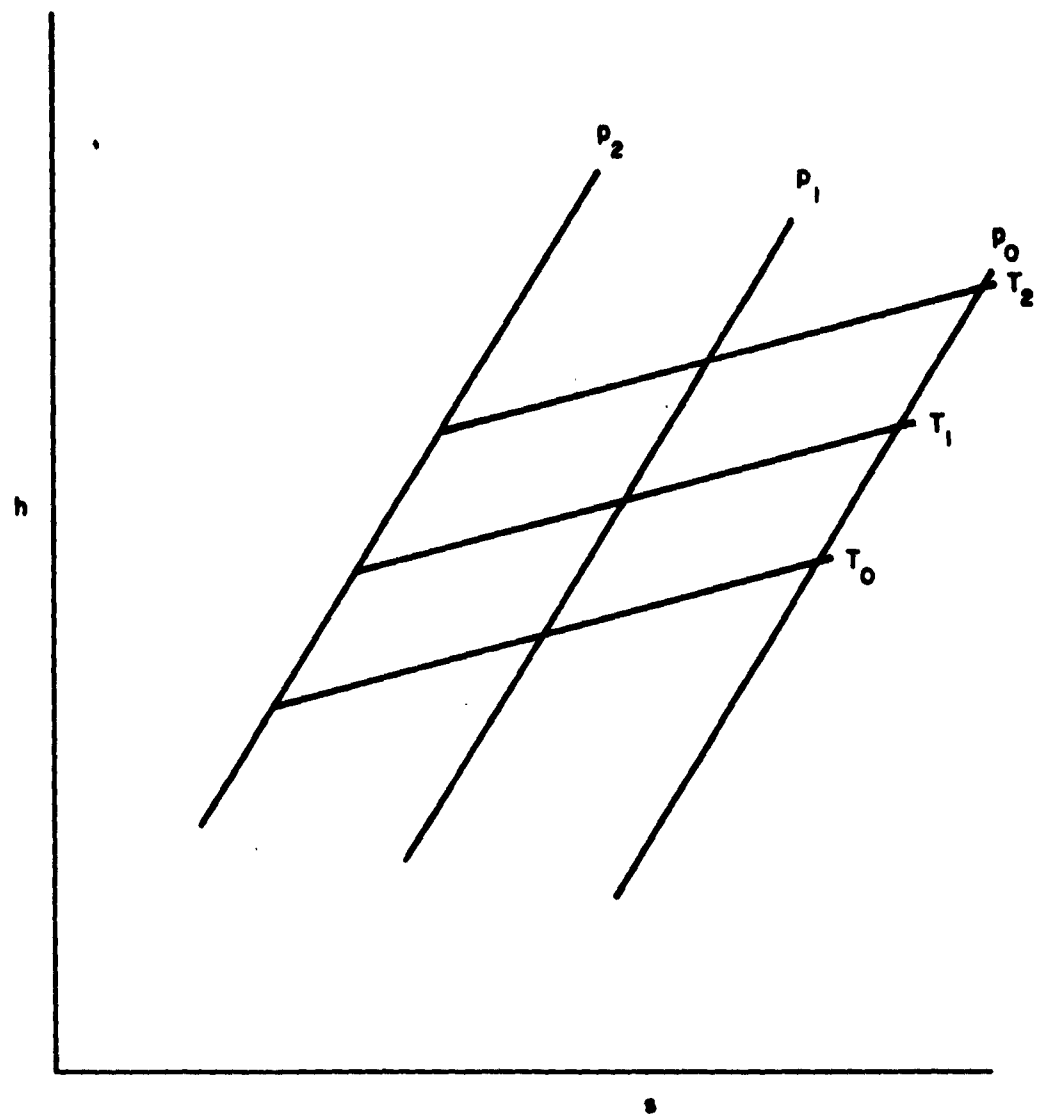


Fig. 2. Mollier Diagram

Since

$$N_s c_v^s = N_s c_p^s \quad (30)$$

and

$$c_p - c_v = \frac{R}{M} \quad (31)$$

then Eq. (29) is

$$\gamma = \frac{N_g c_p^g + N_s c_p^s}{N_g c_p^g - N_g \frac{R}{M} + N_s c_p^s} = \frac{c_p^t}{c_p^t + X_g \frac{R}{M}} \quad (32)$$

where

c_p^t = total specific heat of mixtures

N = weight of gas or solid

X_g = weight fraction of gases

M = molecular weight of mixture

Thus, the M used in a two-phase system is actually M/X_g .

G. Theoretical Rocket Propellant Performance Calculations

The solution of complex chemical equilibria is a fundamental requirement for the computation of theoretical rocket propellant performance. Every parameter of performance may be computed from a thermodynamic analysis of combustion products at selected pressure planes within the thrust chamber.

1. Performance Parameters

Generally, performance parameters which characterize a given propellant system are

- a) I_s specific impulse
- b) c^* characteristic velocity

c) C_F thrust coefficient

d) ϵ area ratio

Items (a) and (c) are a function of the area ratio, and it is usually desired that they be tabulated at numerous pressure ratios in order to predict altitude and vacuum performance. Also, it is advantageous to include tabular material for the calculation of performance resulting from nonoptimum expansion.

2. Specific Impulse

Specific impulse is defined and calculated from the relation

$$I_s = \frac{u_e}{g} + \frac{A_e}{\dot{m}} (p_e - p_o) \quad (33)$$

Optimum specific impulse is established when the static pressure at the nozzle exit is equal to the ambient pressure, and Eq. (33) is

$$I_{opt} = \frac{u_e}{g} \quad (34)$$

When the thrust chamber is at a high altitude and the ambient pressure approaches a vacuum, Eq. (33) is

$$I_{vac} = \frac{u_e}{g} + \frac{A_e p_e}{\dot{m}} \quad (35)$$

Both I_{opt} and I_{vac} are a function of the nozzle expansion ratio (ϵ); the latter is defined by

$$\epsilon = \frac{A_e}{A_t} \quad (36)$$

Because the rocket engine is a heat engine in which the kinetic energy of the jet is created at the expense of combustion product enthalpy, it can easily be shown that

$$I_{\text{opt}} = \sqrt{\frac{2J}{g}} \sqrt{h_c - h_e} \quad (37)$$

The calculation of I_{opt} from Eq. (37) involves the difference in combustion product enthalpy between the chamber and the exit pressure plane. The calculation proceeds on the basis of selecting a chamber pressure and assigning the ambient pressure to the pressure at the exit plane of the nozzle. Calculations are made with the following assumptions:

- a) Propellants are injected into a combustion chamber at a prescribed chamber pressure.
- b) Propellants are transformed adiabatically and isenthalpically into their combustion products at the prescribed chamber pressure.
- c) Combustion is complete, and a mixture results which can be described by the perfect gas law.
- d) Combustion products enter a de Laval nozzle; the contraction ratio (A_e/A_t) is infinite, and the velocity of gases entering the convergent portion of the throat is negligible.
- e) Jet velocity at the throat is equal to the local speed of sound.
- f) Expansion through the nozzle is adiabatic isentropic, frictionless, and one-dimensional.
- g) Condensed phases exhibit a negligible volume and are in thermal equilibrium with gas particles while travelling with their identical velocities.

The expansion process may be treated exactly by the methods of classical thermodynamics with the assumptions of either frozen or shifting

equilibrium. For the former, we assume the composition of the chamber combustion products to be invariant with position in the nozzle. With the assumption of shifting equilibrium, combustion product composition continually changes and is required to reflect the temperature change during the nozzle expansion process. All performance parameters may be computed for the conditions of frozen and shifting equilibrium.

3. Area Ratio (ϵ)

Thrust chamber geometry is best characterized by the area ratio, ϵ . Utilizing the equation for the continuity of mass

$$\rho u A = \dot{m} \quad (38)$$

Eq. (36) becomes

$$\epsilon = \frac{(\rho u)_t}{(\rho u)_e} \quad (39)$$

The perfect gas law is

$$\rho = \frac{pM}{RT} \quad (40)$$

and ϵ is then

$$\epsilon = \frac{\left(\frac{pMu}{T}\right)_t}{\left(\frac{pMu}{T}\right)_e} \quad (41)$$

ϵ is seen to involve the evaluation of the properties of combustion products at the throat and exit pressure plane.

Procedures for evaluating throat properties are somewhat complicated, since the throat position is not uniquely known but encompasses only basic thermodynamics. The significance of Eq. (41) is that from a thermodynamic analysis of combustion products at selected stations in the thrust

chamber, data on the design of thrust chambers may be deduced. Given a propellant stoichiometry and enthalpy, chamber pressure, and exit pressure, an optimum impulse can be computed and the area ratio of the thrust chamber which is required to produce that exit pressure may also be computed.

Substituting Eqs. (34), (36), and (38) into Eq. (33)

$$I_{\epsilon} = I_{opt} + \frac{\epsilon}{(\rho u)_t} (p_e - p_o) \quad (42)$$

from which can be computed the specific impulse at any area ratio (viz, exit pressure) and for all conditions of nonoptimum expansion, $p_e \neq 0$. The special case, I_{vac} , namely, $p_o = 0$, is also included. The term $A_e/\dot{m} = \epsilon/(\rho u)_t$ can be expressed in more tractable terms. From Eqs. (34), (38), and (40),

$$\frac{A_e}{\dot{m}} = \left(\frac{RT}{pMu} \right)_e = \left(\frac{RT}{pM} \right)_e \frac{1}{I_{opt} g} \quad (43)$$

Thus, nonoptimum specific impulse can be computed but without specification of ϵ . However, the specification of the area ratio for optimum or nonoptimum specific impulse will always involve the determination of throat properties since ϵ can only be derived from Eq. (41).

4. Derived Performance Parameters - Thrust Coefficient and Characteristic Velocity

For reasons peculiar to the experimental evaluation of a propellant system in a thrust chamber, it is convenient to define parameters which yield insight into the efficiencies of the combustion and expansion process. Three parameters associated with the thrust chamber which may be experimentally measured are the chamber pressure, throat area, and propellant weight flow. As an excellent approximation for a given throat area, the chamber pressure is directly proportional to the propellant weight flow,

$$p_c \propto \frac{\dot{m}}{A_t} \quad (44)$$

Note that the term $p_c A_t / \dot{m}$ has the dimension of seconds, which are those of specific impulse; and we intuitively conclude that the term could be proportional to specific impulse. Utilizing the acceleration of gravity we find the familiar proportionately constant c^*

$$c^* = \frac{p_c A_t g}{\dot{m}} \quad (45)$$

to have the dimensions of velocity.

The characteristic velocity, c^* , has appeared quite often in the rocket literature and has been the source of much misunderstanding. Much of the confusion associated with the interpretation of c^* could be avoided if its lack of fundamental significance could be kept in mind. Unfortunately, c^* is neither the velocity of the jet at the throat nor at the exit plane, and the product of chamber pressure and throat area has no particular significance. We find Eq. (45) to be a general equation which states that for a given throat area and chamber pressure, propellant systems with higher c^* require less flow rate to produce a given chamber pressure. Equations (44) and (45) are statements of a relationship between chamber pressure and propellant flow rate for a given propellant system. The value of the parameter c^* is that while Eq. (45) may be evaluated experimentally, it may also be evaluated theoretically from a thermodynamic analysis of the propellants, and the results can be compared. Thus, one obtains an experimental indication of whether the particular design of hardware (injector or thrust chamber) permits the realization of near theoretical results. Use of Eqs. (38), (40), and (45) yields

$$c^* = p_c \left(\frac{RT}{pM} \right)_t \frac{g}{u_t} \quad (46)$$

c^* is a single valued function of propellant stoichiometry inlet conditions and chamber pressure and is independent of processes which take place beyond the throat. I_s is a function of propellant stoichiometry and chamber

pressure but includes the contribution of the expansion process. We define the coefficient of thrust

$$C_F = \frac{I_s g}{c^*} \quad (47)$$

and

$$I_s = \frac{c^* C_F}{g} \quad (48)$$

We define c^* and C_F to approximately separate the combustion and expansion efficiencies. Like I_s and c^* , C_F may be computed for both frozen and shifting equilibrium.

In general, c^* , which is determined experimentally, is less than c^* theoretical, while the reverse is true for the thrust coefficient. The reason is that combustion is usually not complete in the chamber and will occur to some extent in the nozzle. The result is a somewhat lower than theoretical chamber pressure. Hence, the experimental c^* is lower than theoretical, while the enthalpy converted to velocity in the nozzle is augmented by an additional enthalpy of combustion. It should be realized that the thrust coefficient is determined indirectly; thrust, chamber pressure, and propellant weight flow are measured directly, and the thrust coefficient is computed.

5. Theoretical Rocket Performance Printout

Tables 24 - 28 illustrate the output format of the Shifting Equilibrium Theoretical Rocket Performance Programs. Input data, such as propellant chemical formulas and heats of formation, are reiterated. Mass balance sheets are then produced, and propellant components are listed in weight per cent, moles, and mole per cent. A list of the combustion products selected and their heats of formation (kcal/mole) follows.

Table 24

REFERENCE DOBBINS P 619

Table 25
Products Selected from Thermodata Tape
 AlH_3/O_2

PRODUCTS CHOSEN ARE THE FOLLOWING

H	HEAT OF FORMATION	52.09024620
C	HEAT OF FORMATION	59.55014181
AL	HEAT OF FORMATION	78.59360123
OH	HEAT OF FORMATION	10.05754995
ALOH	HEAT OF FORMATION	-2.07924271
ALH	HEAT OF FORMATION	62.80041885
H2	HEAT OF FORMATION	0.
H2O	HEAT OF FORMATION	-57.79524899
AL0	HEAT OF FORMATION	17.98375702
AL20	HEAT OF FORMATION	-36.87511876
O2	HEAT OF FORMATION	0.
AL202	HEAT OF FORMATION	-100.00292587
O3	HEAT OF FORMATION	33.99998856
AL2	HEAT OF FORMATION	106.14785004
AL203	COND	-400.60649872
AL	COND	-0.00000191

Table 26
Thermodynamic Conditions for Each of 24 Expansion Planes

THERMC DATA LIBRARY TAPE 43 4/2/62

EXPANSION PLANE NO. 1
CHAMBER PRESSURE 1000 PSIA

TABLE ONE
THERMODYNAMIC CONDITIONS FOR EACH EXPANSION PLANE

PLANE NO.	CHAMBER PRESSURE (PSIA)	TEMPERATURE (°K)	DENSITY (G/CM ³)	ENTHALPY (KCAL/GM)	ENTROPY (KCAL/GM-DEG K)	CP (KCAL/GM-DEG K)	COND MCLES/100 GM
1	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
2	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
3	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
4	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
5	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
6	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
7	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
8	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
9	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
10	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
11	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
12	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
13	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
14	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
15	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
16	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
17	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
18	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
19	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
20	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
21	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
22	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
23	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0
24	1000	333.3	0.00126	7714.284	581.362	7289.5	7099.0

COMPOSITION-MCLES PER 100 GRAMS PROPELLANT

PLANE NO.	AL	OH	ALCH	ALC	AL2O	C2
1	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
2	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
3	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
4	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
5	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
6	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
7	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
8	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
9	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
10	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
11	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
12	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
13	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
14	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
15	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
16	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
17	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
18	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
19	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
20	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
21	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
22	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
23	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000
24	0.45474	0.05170	0.00085	0.00015	0.00015	0.00000

Table 26 (continued)
Thermodynamic Conditions for Each of 24 Expansion Planes

THEMOC DATA LIBRARY TAPE 43 4/2/62

REFERENCE ORIGIN: 7.619
CHAMBER PRESSURE: 1000 PSIA

TABLE ONE
THERMODYNAMIC CONDITIONS FOR EACH EXPANSION PLANE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
W (CAL/GM)	6922.2	6867.7	6824.1	6707.0	6666.9	6633.5	6604.9	6580.4																
S (CAL/GM-DEG K)	2.619	2.619	2.619	2.619	2.619	2.619	2.619	2.619																
CP (CAL/GM)	1.281	1.227	1.184	1.068	1.028	0.996	0.968	0.924																
COND MCLES/100 GM	0.50340	0.50759	0.51053	0.51669	0.51823	0.51931	0.52008	0.52108																

COMPOSITION-MCLES PER 100 GRAMS PROPELLANT

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
AL	0.03098	0.05023	0.04960	0.04769	0.04693	0.04626	0.04566	0.04459																
ON	0.00131	0.00093	0.00069	0.00028	0.00019	0.00014	0.00011	0.00006																
ALCH	0.00010	0.00008	0.00006	0.00003	0.00003	0.00002	0.00002	0.00001																
ALC	0.00159	0.00127	0.00105	0.00057	0.00045	0.00036	0.00030	0.00021																
AL20	0.56745	0.56398	0.56160	0.55698	0.55599	0.55537	0.55499	0.55468																
AL202	0.00003	0.00002	0.00002	0.00001	0.00001	0.00001	0.00001	0.00000																

Table 26 (continued)
Thermodynamic Conditions for Each of 24 Expansion Planes

THEMO DATA LIBRARY TAPE 43 4/2/62

TABLE ONE
THERMODYNAMIC CONDITIONS FOR EACH EXPANSION PLANE

	PLANE 1	PLANE 2	PLANE 3	PLANE 4	PLANE 5	PLANE 6	PLANE 7	PLANE 8	PLANE 9	PLANE 10	PLANE 11	PLANE 12	PLANE 13	PLANE 14	PLANE 15	PLANE 16	PLANE 17	PLANE 18	PLANE 19	PLANE 20	PLANE 21	PLANE 22	PLANE 23	PLANE 24	
M (CAL/GP)	6480.9	6352.6	6231.2	6159.9	6111.1	6074.5	6010.9	5967.7																	
S (CAL/GP-DEG K)	2.619	2.619	2.619	2.619	2.619	2.619	2.619	2.619																	
CP (CAL/GM)	0.853	0.789	0.790	0.728	0.682	0.650	0.602	0.576																	

	PLANE 1	PLANE 2	PLANE 3	PLANE 4	PLANE 5	PLANE 6	PLANE 7	PLANE 8	PLANE 9	PLANE 10	PLANE 11	PLANE 12	PLANE 13	PLANE 14	PLANE 15	PLANE 16	PLANE 17	PLANE 18	PLANE 19	PLANE 20	PLANE 21	PLANE 22	PLANE 23	PLANE 24	
COND MGLES/100 GM	0.52208	0.52236	0.52278	0.52320	0.52326	0.52321	0.52300	0.52277																	

COMPOSITION-PCLES PER 100 GRAMS PROPELLANT

	PLANE 1	PLANE 2	PLANE 3	PLANE 4	PLANE 5	PLANE 6	PLANE 7	PLANE 8	PLANE 9	PLANE 10	PLANE 11	PLANE 12	PLANE 13	PLANE 14	PLANE 15	PLANE 16	PLANE 17	PLANE 18	PLANE 19	PLANE 20	PLANE 21	PLANE 22	PLANE 23	PLANE 24	
CH	0.00002	0.00001	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000																	
ALCH	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000																	
ALN	0.00302	0.00245	0.00199	0.00190	0.00186	0.00184	0.00182	0.00182																	

	PLANE 1	PLANE 2	PLANE 3	PLANE 4	PLANE 5	PLANE 6	PLANE 7	PLANE 8	PLANE 9	PLANE 10	PLANE 11	PLANE 12	PLANE 13	PLANE 14	PLANE 15	PLANE 16	PLANE 17	PLANE 18	PLANE 19	PLANE 20	PLANE 21	PLANE 22	PLANE 23	PLANE 24	
AL20	0.55491	0.55605	0.55510	0.55476	0.55492	0.55520	0.55597	0.55429																	
AL202	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000																	
AL2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001																	

Table 27
Optimum Specific Impulse Tabulation

THEME DATA LIBRARY TAPE 43 4/2/62

TABLE TWO
C* = 6042 FT/SEC

1.0000	1000.0000	3003.7	7661.27	1.1163	0.	0.	0.
1.0400	961.5385	3791.4	7648.60	1.1162	2.3403	0.1765	33.15
1.4023	293.9188	3435.9	7289.46	1.1154	1.2481	0.9577	179.86
6.9046	146.9594	3239.1	7098.95	1.1169	1.8885	1.1777	221.19
10.2069	97.9729	3126.3	6993.77	1.1185	2.4914	1.2832	240.99
20.4137	48.9867	2936.1	6824.13	1.1222	4.1303	1.4370	269.89
34.0229	29.3920	2797.1	6707.01	1.1256	6.0949	1.5342	288.15
40.8275	24.4933	2747.7	6666.86	1.1270	7.0197	1.5662	294.15
100.0000	10.0000	2505.0	6480.89	1.1349	14.2280	1.7064	320.48
200.0000	5.0000	2371.2	6352.56	1.1393	25.4864	1.7967	337.45
1000.0000	1.0000	2076.4	6074.53	1.1543	100.7116	1.9784	371.57
1500.0000	0.6667	1968.8	6010.86	1.1612	140.1726	2.0177	378.95
2000.0000	0.5000	1892.4	5967.72	1.1659	177.1835	2.0439	383.87

Table 28
Altitude Specific Impulse

THERMC DATA LIBRARY TAPE 43 4/2/62

TABLE THREE

2.0000	7.4192	226.25	50.63	0.38	276.88	1.2047	1.4762
3.0000	13.2326	252.36	42.58	0.56	294.94	1.3437	1.5704
4.0000	19.5596	268.21	38.41	0.75	306.62	1.4281	1.6326
7.0000	40.6800	294.03	32.32	1.31	326.35	1.5656	1.7376
8.0000	48.2773	299.47	31.12	1.50	330.59	1.5945	1.7602
9.0000	56.1055	304.10	30.13	1.69	334.22	1.6192	1.7796
12.0000	80.7187	314.78	27.92	2.25	342.70	1.6760	1.8247
13.0000	89.4599	317.25	27.29	2.44	344.54	1.6892	1.8345
14.0000	98.0377	319.90	26.82	2.63	346.72	1.7033	1.8461
17.0000	124.0584	326.76	25.74	3.19	352.50	1.7398	1.8769
18.0000	132.8278	328.69	25.45	3.38	354.15	1.7501	1.8856
19.0000	141.6450	330.45	25.19	3.57	355.64	1.7594	1.8936
22.0000	168.8478	332.85	24.47	4.13	357.33	1.7723	1.9026
23.0000	177.7663	334.23	24.30	4.32	358.53	1.7796	1.9090
24.0000	186.6984	335.56	24.14	4.51	359.71	1.7867	1.9152

Table 28 (continued)
Altitude Specific Impulse

THERMC DATA LIBRARY TAPE 43 4/2/62

TABLE THREE

27.0000	213.5770	339.26	23.74	5.07	363.00	1.8064	1.9328
28.0000	222.5639	340.39	23.63	5.26	364.02	1.8124	1.9382
29.0000	231.5645	341.48	23.52	5.45	365.00	1.8182	1.9434
32.0000	258.6483	344.44	23.24	6.01	367.68	1.8340	1.9577
33.0000	267.7037	345.33	23.15	6.20	368.49	1.8387	1.9620
34.0000	276.7727	346.18	23.07	6.39	369.25	1.8432	1.9660
37.0000	300.6509	346.18	23.11	6.95	369.29	1.8432	1.9663
38.0000	309.8335	346.86	23.03	7.14	369.90	1.8469	1.9695
39.0000	319.0865	347.53	22.96	7.32	370.49	1.8504	1.9727
42.0000	347.2682	349.48	22.71	7.89	372.20	1.8608	1.9818
43.0000	356.8029	350.11	22.63	8.08	372.75	1.8642	1.9847
44.0000	366.4081	350.73	22.55	8.26	373.28	1.8674	1.9875
47.0000	395.6463	352.50	22.31	8.83	374.01	1.8769	1.9937
48.0000	405.5332	353.07	22.23	9.01	375.30	1.8799	1.9983
49.0000	415.4905	353.63	22.15	9.20	375.77	1.8829	2.0008

The problem solved in the tables illustrates the typical three-table shifting equilibrium output format. While the selection of the chamber pressure is infinitely variable, computations are executed at 24 pressure ratios (Table 26). The initial pressure is that within the combustion chamber whereas the fifth pressure locates the exact position and conditions at the throat. At every pressure, the temperature, enthalpy, entropy, heat capacity, isentropic exponent (GAMMA), product molecular weights, and the concentration of combustion products are printed.

Table 27 lists the rocket performance data. Characteristic velocity is tabulated as is optimum specific impulse, expansion ratio (EPSILON), and thrust coefficient (CF) as a function of pressure ratio.

Table 28 lists altitude performance parameters as a function of 50 unit area ratios and is utilized to read the thrust coefficient (CF EPS) and specific impulse (I EPS) for an ambient pressure of zero as a function of area ratio. Optimum specific impulse (I OPT) is tabulated at the unit area ratio. The table affords the rapid and accurate calculation of specific impulse under any set of optimum and nonoptimum area ratios and altitude conditions. The exact equation for these effects is

$$\begin{aligned}
 I \text{ EPS} &= I \text{ OPT} + A - B p_o \\
 &= \frac{u_e}{g} + \left(\frac{RT}{Mu} \right)_e - \left(\frac{RT}{pMu} \right)_e p_o \\
 &= I \text{ OPT} + \frac{p_e c^{*\epsilon}}{p_c g} - \frac{p_o c^{*\epsilon}}{p_c g}
 \end{aligned} \tag{49}$$

Table 29 illustrates a portion of the thermodynamic properties of the propellant system N_2O_4 with BeH_2 . Solution was obtained with the presence of three condensed phases.

This image is a vertical strip of a document page, heavily degraded and noisy. It shows fragments of text and a large, dark, irregular shape, possibly a stamp or a large mark, which is mostly illegible due to the poor quality of the scan.

TEMPERATURE CONDITIONS FOR EACH EXTENSION, SHOW

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COMBUSTION HEELS PER 100 GRAMS PROPELLANT

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ACKNOWLEDGEMENT

The authors are indebted to R. L. Wilkins of the Aerodynamics and Propulsion Research Laboratory for frequent helpful discussions.

<p>Aerospace Corporation, El Segundo, California. THE AEROSPACE CORPORATION COMPUTER PROGRAMS FOR THE SOLUTION OF MULTIELEMENT CHEMICAL EQUILIBRIA. (UNCLASSIFIED TITLE), prepared by S. A. Greene and H. J. Vale. 28 June 1962. [78]p. incl. illus. (Report TDR-69(2240-51)TR-2; DCAS-TDR-62-138) (Contract AF 04(695)-69) Unclassified report</p> <p>Work has been completed on a generalized method for the analytical solution of complex multielement chemical equilibria under all conditions of pressure, temperature, and mass balance. The programs are written for the IBM 7090 and use a unique technique of majors and minors to guarantee automatic convergence. Variations of the basic solution method are applied to problems in chemical synthesis, thermal stability, and chemical compatibility. The programs are also used to obtain theoretical rocket propellant performance and Mollier diagrams.</p>	UNCLASSIFIED
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